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Chapter 4

Evaluation of Antimicrobial Efficiency of Bipyrimidines Using Zeolite as a Green Catalyst in Biphasic System

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ABSTRACT

In the present study, we have designed and synthesized a new series of bipyrimidines by simple condensation and screened them for their in vitro antimicrobial activities. Current research has depicted the efforts towards the utilization of biphasic reaction systems in the synthesis of a variety of heterocycles. This shows the remarkable importance of the monophasic solvent system. A simple, green and efficient catalytic condensation process has been developed to synthesize the series of 2-amino-6-substituted- 4,6-diphenyl-3',4,4',5-tetrahydro[4,5'-bipyrimidine]-2'(1*H*)-one (3a- *j*) hybrids. The catalytic route was investigated efficiently in the presence of NaY zeolite in an organic-aqueous (dichloromethane-water) solvent system. In this method, biphasic solvent systems were explored for suitable applicability where catalyst exhibits remarkable reactivity. The synthesized scaffolds of bipyrimidines were studied as anti-microbial agents. The investigation of antimicrobial screening data revealed that among 10 compounds screened, compounds 3d, 3e, 3f and 3i demonstrated very good activity as compared to standard drugs and the remaining compounds showed good to moderate inhibition activities.

Synthesized compounds were screened for their *in vitro* antibacterial activity against *Staphylococcus aureus*, *E. coli* and *Pseudomonas aurigenosa* and also antifungal activity against the opportunistic pathogens *Candida albicans* and *Aspergillus niger*.

Keywords: Bipyrimidines; zeolite; dichloromethane-water biphasic system; antimicrobial activity.

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1. INTRODUCTION

Green synthesis of zeolites can be classified into four main categories: (1) synthetic methods that do not require a template or use a recyclable, inexpensive, or renewable template; (2) synthesis of zeolites that use sustainable silicon or aluminum sources; (3) solvent-free methods; and (4) facile synthesis methods, e.g., microwave heating to shorten the crystallization time, solid phase (or quasi-solid phase) synthesis to promote product yield, or continuous-flow synthesis to achieve high productive efficiency [1,2]. Bipyrimidines hybrids play an essential role in several biological processes and have considerable chemical and pharmacological importance [3]. A large number of bipyrimidine derivatives are reported to be antimicrobial [4], anticancer [5], antiviral [6], anti-inflammatory [7], antifungal [8], analgesic [9], anticonvulsant [10], antioxidant [11], antitubercular, antimalarial [12] and antileishmanial [13].

Zeolite X is a highly versatile molecular sieve with a pore size of 7.4 Å from the faujasite family of zeolites whose, three-dimensional pore structure and solid acidity make it useful asa catalyst in the synthesis of analogues of several *N*-heterocycles[14,15,3]. Because of their unique properties, which include controlled variability, thermal stability, reusability, and environmental friendliness, zeolites are the most important catalysts in green chemistry. The efforts to use a biphasic reaction system in the synthesis of various heterocycles have been documented in current research. This shows the remarkable importance of the monophasic solvent system. The biphasic solvent system allows easy separation and reusability of the reactive aqueous phase containingspent homogeneous or heterogeneous catalysts [3]. The recent work from various research groups indicated that biphasic reaction systems showed significant advantages in protecting the products from further degradation by extracting the products produced from the monophasic solvent, simplifying the separation steps to achieve the final products, minimizing the side reactions and increasing the overall yield [16,17,3].

We opted for an approach for the development of an easy, efficient, green and clean method for the synthesis of 2-amino- 6-substituted-4,6-diphenyl-3',4,4',5-tetrahydro[4,5'-bipyri- midine]-2' (1H)-one analogues (3a-j). The rarity of reports in the catalytic synthesis of bipyrimidines in a biphasic solvent system, the work aims to study the beneficial approach in yields of bipyrimidines in DCM-water optimized phase using zeolite as a catalyst [3]. In the present study, we have designed and synthesized a new series of bipyrimidines by simple condensation and screened them for their in vitro antimicrobial activities where 3d, 3e, 3f and 3i were found to exhibit excellent potent activity as antibacterial and antifungal agents. Other compounds possessed moderate to low activity.

2. EXPERIMENTAL

Bipyrimidines were synthesized by using analytical grade substituted chalcone and guanidine hydrochloride (S.D. Fine Chemicals, 98 %). Zeolite, dichloromethane, ethyl acetate and n-hexane were obtained from Qualigen India Ltd. Mumbai.

Melting points were determined by open capillary method and are uncorrected. All solvents were distilled and dried prior to use [3]. TLC was performed on silica gel G and the spots were exposed to iodine vapours for visualization. A mixture of n-hexane and ethyl acetate (7:3) was used as an eluent. 1H NMR and 13C NMR spectra were recorded in $CDCl_3$ on a Brucker AC 400 (MHz) instrument. Chemical shifts are reported in ppm using TMS as the internal standard. IR spectra were obtained on a Perkin Elmer 1800 spectrophotometer using KBr discs and mass spectra were measured with Shimadzu gas chromatograph coupled with QP5050 Spectrometer at 1-1.5 eV. CHN elemental analysis was carried out with Perkin Elmer 300A elemental analysis [3].

In vitro Antibacterial and antifungal activities: All the series of synthesized compounds were evaluated for their efficacy against the clinically isolated microorganisms as Escherichia coli (ATCC 25922), *Pseudomonas aeruginonasa* (ATCC 85327) (Gram-negative bacteria) *Staphylococcus aureus* (ATCC 29213) (Gram-positive bacteria), *Candida albicans* (ATCC 102310) and *Aspergillus niger* (ATCC 439). The preliminary antimicrobial activities of the compounds 3a-j were tested using the cup-plates method [18,19,3]. The compounds to be screened were dissolved in DMSO at different concentrations *viz*. 12.5, 25, 50 and 100µg/mL. The plates were incubated at 37 °C for 24 h, the control was similarly maintained with 1 mL of DMSO and the zonesof inhibition of bacterial and fungal growth were measured inmm. Ampicillin and ketoconazole were used as the standarddrugs. The inoculated plates were incubated at 37 °C for 24 hin the case of bacteria and 48 h in the case of fungus. The zoneof inhibition was compared with the standard drugs [3].

The minimum inhibitory concentrations (MIC) of compounds were tested using the microdilution susceptibility method [16]. The chemical stock solutions of all the compounds andreference drugs were prepared by dissolving 1000 µg in 5 mL DMSO. A series of dilutions were prepared as 100, 50, 25 and 12.5 µg/mL. The solutions with no turbidity were considered as MIC for tested compounds [3].

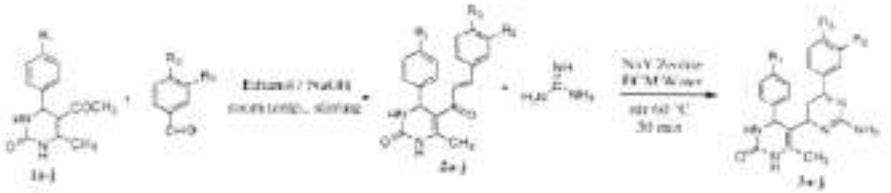
General procedure for the synthesis of 5-cinnamoyl-6-methyl- 4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (2a): The synthesisof chalcones was carried out via Claisen-Schmidt condensation. A mixture of 5-acetyl-6-methyl-4-phenyl-3,4-dihydro- pyrimidine-2(1*H*)-one (1 mmol, 0.214 g) and benzaldehyde (1 mmol, 0.106 g) was dissolved in 10 mL of ethanol in 250 mL round bottom equipped with a magnetic stirrer. Then 20 mL NaOH solution (8 g in 20 mL H_2O) was added dropwiseto the reaction mixture with vigorous stirring for 0.5 h at roomtemperature. The reaction mixture was kept overnight. The reaction mixture was neutralized by adding dilute HCl wherebythe precipitation occurred. The product was filtered and recrystallized by ethanol. The physicochemical analysis of the synthesized compounds is shown in Table 1 [3].

General procedure for thesynthesis of 2-amino-6-methyl-4,6-diphenyl-3',4,4',5-tetrahydro-[4,5'-bipyrimidine]- 2' (1H)-one (3a): In a 50 mL of round bottom flask 5-cinnamoyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**2a**) (5 mmol, 1.65 g) and zeolite (30 mol %, 0.573 g) were thoroughlymixed in dichloromethane and were stirred for few minutes. Guanidine hydrochloride (10 mmol, 0.95 g) dissolved in water

was poured into a round bottom flask of reaction mixture. The solution was now stirred in organic-water phases as reaction media at 60 °C for 0.5 h (Scheme-I) [3]. The extent of the reaction was monitored by TLC. After the completion of the reaction, the product was extracted from biphasic solvents as a solid material by filtration. The solvents were separated by a separating funnel and water was evaporated to get the zeolite for the next run. The product (3a) obtained was subjected to recrystallization by ethanol. The physico-chemical analysis of the synthesized compounds are shown in Table 2 [3].

Table 1. Synthesized of Substituted 5-Cinnamoyl-6-Methyl-4-Phenyl-3,4 Dihydropyrimidin-2(1H)-One (2a-j)

Compd.	R_1	R_2	Yield(%)	Time (min)	m.p. (°C)
2a	-H	-H	83	90	160
2b	-H	$-NO_2$	79	120	215
2c	-H	$-OCH_3$	85	105	220
2d	$-OCH_3$	$-OCH_3$	80	110	200
2e	-Cl	-H	82	105	173
2f	-H	-Cl	82	105	168
2g	$-NO_2$	-H	85	120	210
2h	$-OCH_3$	$-NO_2$	86	115	220
2i	-Cl	$-OCH_3$	87	135	208
2j	$-NO_2$	$-OCH_3$	84	130	217



R_1 = H, NO_2, OCH_3, Cl; R_2 = H; R_3 = H, NO_2, OCH_3, Cl

Scheme-I

Table 2. synthesized of bipyrimidines of 2-amino-6- substituted-4,6-diphenyl-3',4,4',5-tetrahydro- [4,5'-bipyrimidine]-2'(1h)-one (3a-j)

Compd.	R_1	R_2	R_3	Yield(%)	Time(min)	m.p.(°C)
3a	-H	-H	-H	89	30	198
3b	-H	-H	$-NO_2$	86	34	195
3c	-H	-H	$-OCH_3$	85	36	190
3d	$-OCH_3$	-H	$-OCH_3$	84	30	222
3e	-Cl	-H	-H	87	45	202
3f	-H	-H	-Cl	83	34	188
3g	$-NO_2$	-H	-H	87	48	201
3h	$-OCH_3$	-H	$-NO_2$	86	56	265
3i	-Cl	-H	$-OCH_3$	85	47	226
3j	$-NO_2$	-H	$-OCH_3$	86	45	233

2-Amino-6-methyl-4,6-diphenyl-3',4,4',5-tetrahydro-[4,5'-bipyrimidine]-2'(1*H*)-one (3a) [3]: Yellow-colored solid, yield: 89%; m.p. 198 °C. IR (KBr, ν_{max}, cm^{-1}): 3286, 1612,1454, 1074. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.9-7.8 (m,10H, arom.), 8.6 (s, 1H, -NH), 8.7 (s, 1H, -NH), 3.9 (s, 2H, $-NH_2$), 2.4 (s, 3H, $-CH_3$), 2.68-2.70 (d, J = 10.68 Hz, 2H, $-CH_2$), 3.32-3.34 (t, 1H, -CH), 5.6 (s, 2H, -CH). ^{13}C NMR ($CDCl_3$, δ ppm): 15.2, 35.8, 40.9, 58.6, 114.4, 120.9, 127.1, 128.7,131.0, 139.9, 141.8, 149.5, 153.6, 163.7. MS (70 eV): m/z =359.17 [M+]. Anal. Calcd. (found) % for $C_{21}H_{21}N_5O$ m.w. 359.17: C, 70.17 (70.15); H, 5.89 (5.86); N, 19.48 (19.45); O,4.45 (4.43).

2-Amino-6-methyl-6-(4-nitrophenyl-4-phenyl-3',4,4',5-tetrahydro[4,5'-bipyrimidine]-2'(1*H*)-one (3b) [3]: Light yellow coloured solid, yield: 86 %, m.p. 195 °C, IR (KBr, ν_{max}, cm^{-1}): 3285, 1611, 1450, 1072. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.8-7.2 (m, 9H, arom.), 8.1 (s, 1H, -NH), 8.3 (s, 1H, -NH), 3.9 (s, 2H, $-NH_2$), 2.3 (s, 3H, $-CH_3$), 2.58-2.60 (d, J = 10.68 Hz, 2H, $-CH_2$), 3.32-3.34 (t, 1H, -CH), 5.6 (s, 2H, -CH). ^{13}C NMR ($CDCl_3$, δ ppm): 14.6, 35.0, 40.3, 56.4, 58.7, 115.1, 123.2, 125.2, 127.9, 128.8, 141.7, 141.8, 145.5, 149.5, 154.3, 164.7. MS (70 eV): m/z = 404 [M+]. Anal. Calcd. (found) % for $C_{21}H_{20}N_6O_3$, m.w. 404.14: C, 62.37 (63.65); H, 4.98 (4.97); N, 20.78 (20.75); O,11.87 (11.85).

2-Amino-6-(4-methoxyphenyl)-6-methyl-4-phenyl-3',4,4',5-tetrahydro[4,5'-bipyrimidine]-2'(1*H*)-one (3c) [3]: Dark brown coloured solid, yield: 85 %, m.p. 190 °C. IR (KBr, ν_{max}, cm^{-1}): 3282, 1613, 1452, 1072. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.9-7.4 (m, 9H, arom.), 8.5 (s, 1H, -NH), 3.9 (s, 2H, - NH_2), 2.5 (s, 3H, - CH_3), 2.83-2.85 (d, J = 10.68 Hz, 2H, - CH_2), 3.22-3.24 (t, 1H, -CH), 5.4 (s, 2H, -CH), 3.2 (s, 3H, - OCH_3). ^{13}C NMR ($CDCl_3$, δ ppm): 14.6, 35.1, 40.3, 56.7, 58.8, 113.1, 115.0, 124.7, 126.1, 128.5, 133.6, 141.3, 149.8, 152.3, 163.1, 165.1. MS (70 eV): m/z 389.19 [M+]. Anal. Calcd. (found) % for $C_{22}H_{23}N_5O_2$, m.w. 389.14: C, 67.85 (67.83); H, 5.95 (5.93); N, 17.98 (17.96); O, 8.22 (8.20).

2-Amino-4',6-*bis*(4-methoxyphenyl)-6-methyl-3',4,4',5-tetrahydro[4,5'-bipyrimidine]-2'(1H)-one (3d) [3]: Yellow coloured solid, yield: 84 %, m.p. 222 °C. IR (KBr, ν_{max}, cm^{-1}):3285, 1612, 1453, 1070. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.9-7.9 (m, 8H, arom.), 8.6 (s, 1H, -NH), 4.02 (s, 2H, $-NH_2$), 2.4 (3H, - CH_3), 2.50-2.53 (d, J = 10.68 Hz, 2H, $-CH_2$), 3.32- 3.34 (t, 1H, -CH), 5.5 (s, 2H, -CH), 3.6 (s, 3H, $-OCH_3$). $^{13}CNMR$ ($CDCl_3$, δ ppm): 14.1, 35.1, 39.8, 55.9, 58.8, 114.2, 115.0, 124.6, 126.7, 128.9, 133.2, 139.9, 141.8, 149.5, 152.8, 159.9, 162.4, 164.1. MS (70 eV): m/z 419.19 [M+]. Anal. Calcd. (found) % for $C_{23}H_{25}N_5O_3$, m.w. 419.18: C, 65.85 (65.82); H,6.01 (6.01); N, 16.70 (16.68); O, 11.44 (11.42).

2-Amino-4-(4-chlorophenyl)-6-methyl-6-phenyl-3',4,4',5-tetrahydro[4,5'-bipyrimidine]-2'(1*H*)-one (3e) [3]: Pale yellow coloured solid, yield: 87 %, m.p. 202 °C. IR (KBr, ν_{max}, cm^{-1}): 3281, 1610, 1452, 1073. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.3-7.9 (m, 9H, arom.), 8.6 (s, 1H, -NH), 3.9 (s, 2H, - NH_2), 2.1 (s, 3H, $-CH_3$),

2.60-2.63 (d, J = 10.68 Hz, 2H, -CH_2), 3.42-3.44 (t, 1H, -CH), 5.6 (s, 2H, -CH). ^{13}C NMR (CDCl3, δ ppm): 15.2, 35.8, 40.9, 58.6, 114.4, 123.5, 127.1, 128.3, 129.8, 131.3, 139.9, 141.8, 149.5, 153.6, 163.7. MS (70 eV): m/z = 393.14 [M$^+$]. Anal. Calcd. (found) % for $C_{21}H_{20}N_5OCl$, m.w. 393.12: C, 64.04 (64.02); H, 5.12 (5.10); N, 17.78 (17.75); O,4.06 (4.03); Cl, 9.00 (9.90).

2-Amino-6-(4-chlorophenyl)-6-methyl-4-phenyl-3',4,4',5-tetrahydro[4,5'-bipyrimidine]-2'(1*H*)-one (3f) [3]: Light yellow coloured solid, yield: 83 %; m.p. 188 °C. IR (KBr, νmax, cm^{-1}): 3283, 1612, 1454, 1073. ^{1}H NMR (400MHz, CDCl3, δ ppm): 7.4-7.8 (m, 9H, arom.), 8.7 (s, 1H, -NH), 3.7(s, 2H, - NH_2), 2.1 (s, 3H, -CH_3), 2.40-2.43 (d, J = 10.68 Hz, 2H, -CH_2), 3.32-3.34 (t, 1H, -CH), 5.7 (s, 2H, -CH). ^{13}C NMR (CDCl3, δ ppm): 15.2, 35.8, 40.9, 58.6, 114.4, 123.6, 127.1, 128.7, 131.0, 135.9, 137.6, 141.8, 149.5, 153.6, 163.7. MS (70 eV): m/z = 393.14 [M+]. Anal. Calcd. (found) % for $C_{21}H_{20}N_5OCl$, m.w.393.14: C, 64.04 (64.02); H, 5.12 (5.10); N, 17.78 (17.75); O,4.06 (4.03); Cl, 5.12 (5.10).

2-Amino-6-methyl-4-(4-nitrophenyl)-6-phenyl-3',4,4',5-tetrahydro[4,5'-bipyrimidine]-2'(1*H*)-one (3g) [3]: Yellow coloured solid, yield: 87 %, m.p. 201 °C. IR (KBr, νmax, cm^{-1}): 3284,1610,1453,1072. ^{1}H NMR (400 MHz, CDCl3, δppm): 7.5-7.9 (m, 9H, arom.), 8.6 (s, 1H, -NH), 8.1 (s, 1H, -NH), 3.9 (s, 2H, -NH_2), 2.2 (3H, -CH3), 2.47-2.50 (d, J = 10.68 Hz, 2H, -CH_2), 3.34-3.32 (t, 1H, -CH), 5.6 (s, 2H, -CH). ^{13}C NMR (75 MHz, CDCl3, δppm): 15.2, 35.8, 40.9, 58.6, 114.4, 123.6, 123.9, 127.1, 128.7, 131.0, 139.9, 146.2, 147.9, 149.5, 153.6, 163.7. MS (70 eV): m/z 404.16 [M$^+$]. Anal. Calcd. (found) % for $C_{21}H_{20}N_6O_3$, m.w. 404.16: C, 62.37 (62.35); H, 4.98 (4.97); N, 20.78 (20.75); O, 11.87 (11.85).

2-Amino-4-(4-methoxyphenyl)-6-methyl-6-(4-nitro-phenyl)-3',4,4',5-tetrahydro [4,5'-bipyrimidine]-2'(1H)-one (3h) [3]: Dark yellow solid, yield: 86 %, m.p. 265 °C. IR (KBr, νmax, cm^{-1}): 3286, 1613, 1453, 1073. ^{1}H NMR (400 MHz, CDCl3, δ ppm): 6.7-7.8 (m, 8H, arom.), 8.6 (s, 1H, -NH), 8.2 (s, 1H, - NH), 4.0 (s, 2H, -NH_2), 2.2 (s, 3H, -CH_3), 2.50-2.53 (d, J = 10.68 Hz, 2H, -CH_2), 3.42-3.44 (t, 1H, -CH), 5.6 (s, 2H, -CH), 3.7 (s, 3H, -OCH_3). ^{13}C NMR (CDCl3, δ ppm): 15.2, 35.8, 40.9, 58.6, 113.1, 114.4, 123.4, 125.5, 127.1, 128.7, 135.7, 146.9, 149.5, 153.6, 158.5, 163.7. MS (70 eV): m/z 434.45 [M$^+$].
Anal. Calcd. (found) % for $C_{22}H_{22}N_6O_4$, 434.42: C, 60.87(60.85); H, 5.10 (4.98); N, 19.34 (19.32); O, 14.73 (14.70).

2-Amino-6-(4-chlorophenyl)-6-methyl-4'-(4-methoxy-phenyl)-6',4,4',5tetrahydro[4,5'-bipyrimidine]-2'(1H)-one(3i) [3]: Yellow coloured solid, yield: 85 %, m.p. 226 °C. IR (KBr,νmax, cm^{-1}): 3286, 1614, 1453, 1074. ^{1}H NMR (400 MHz,CDCl3, δ ppm): 7.0-7.9 (m, 8H, arom.), 8.6 (s, 1H, -NH), 8.0(s, 1H, -NH), 3.9 (s, 2H, -NH_2), 2.3 (s, 3H, -CH_3), 2.50-2.53(d, J = 10.68 Hz, 2H, -CH_2), 3.32-3.34 (t, 1H, -CH), 5.4 (s,2H, -CH), 3.7 (s, 3H, -OCH_3). ^{13}C NMR (CDCl3, δ ppm): 15.2,35.8, 40.9, 56.2, 58.6, 113.9, 114.4, 115.8, 123.7, 124.9, 127.1,128.7, 133.1, 136.5, 138.9, 149.5, 153.6, 158.4, 163.7. MS (70 eV): m/z 423.18 [M$^+$]. Anal.

Calcd. (found) % for $C_{22}H_{22}N_5O_2Cl$, m.w. 423.18: C, 65.17 (65.15); H, 5.72 (5.73); Cl, 8.36 (8.00); N, 17.27 (17.29); O, 8.84 (7.85).

2-Amino-4'-(4-methoxyphenyl)-6'-methyl-6'-(4-nitrophenyl)-3',4,4',5-tetrahydro[4,5'-bipyrimidine]- 2'(1H)-one (3j) [3]: Light yellow solid, yield 86 %, m.p. 233 °C, IR (KBr, ν_{max}, cm^{-1}): 3282, 1610, 1452, 1074. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.7-8.2 (m, 8H, arom.), 8.5 (s, 1H, -NH), 8.5 (s, 1H, -NH), 4.0 (s, 2H, $-NH_2$), 2.2 (s, 3H, $-CH_3$), 2.50-2.53 (d, J = 10.68 Hz, 2H, $-CH_2$), 3.42-3.44 (t, 1H, -CH), 5.6(s, 2H, -CH), 3.7 (s, 3H, $-OCH_3$). ^{13}C NMR (75 MHz, $CDCl_3$,δ ppm): 15.2, 35.8, 40.9, 56.2, 58.6, 113.9, 114.4, 115.8, 124.9,127.1, 128.7, 133.9, 135.7, 149.5, 153.6, 163.7, 165.2. MS (70 eV): *m/z* 423.16 [M$^+$]. Anal. Calcd. (found) % for $C_{22}H_{22}N_5O_2Cl$,m.w. 423.16: C, 62.34 (62.36); H, 5.23 (5.25); N, 16.52 (16.53);Cl, 8.36 (8.35); O, 7.55 (7.55).

3. RESULTS AND DISCUSSION

In a model reaction of 5-cinnamoyl-6-methyl-4-phenyl- 3,4-dihydropyrimidin-2(1*H*)-one (2a) and guanidine hydrochloride in biphasic system of solvents of DCM and water weresubjected to catalytic reaction in presence of NaY zeolite forthe synthesis of 2-amino-6-methyl-4,6-diphenyl-3',4,4',5- tetrahydro[4,5'-bipyrimidine]-2' (1*H*)-one (3a) at 60 °C for 30min stirring [3]. Initially, our efforts focused on delineating a simple, green condensation reaction of 5-cinnamoyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (2a) and guanidine hydrochloridein presence of NaY zeolite to get 2-amino-6-methyl- 4,6diphenyl-3',4,4',5-tetrahydro-[4,5'-bipyrimidine]-2' (1H)- one (3a). We proceeded with an organic solvent of dichloro-methane which came with only 12 % yield. Further, we worked on the reaction with other aprotic solvents as *n*-hexane,toluene, cyclohexane, ethyl acetate and THF, results were unsuccessful. Looking into the disadvantages of the monophasic solvent system, we focused our efforts on the organic-aqueous biphasic system to get better yields of product [20-22,3]. The biphasic solvents play a crucial role in determining the amountof product in catalysis. The first step towards determining the biphasic organic solvents that are immiscible with water, resultsin the minimum number of toxic side products and intermediates with a clean environmental approach [23] (Table-3) [3]. All other permutations generated by varying parameters, such as concentration of zeolite, reaction time for condensation, reaction temperature; and the ratio of the organic-aqueous system led to lower yields.The extensive optimization for the various biphasic systems (Table-3), and DCM-water 1:1 ratio (Table-4) in 30 mol % of catalyst(Table-5) furnished astonishing results with 89 % in yield. The possible explanation for such an amazing behaviour of organic-aqueous reaction media of DCM-water system is due to characteristic properties of DCM as compared to other solvents *i.e.*high polarity, high dielectric constant, high dipole moment and low boiling point of dichloromethane [3].

Table 4 shows that the organic solvent and water ratio had a significant impact on the product yield. To understandthe effect of the organic phase on the yield of the product, the distribution of different ratios of the biphasic system was carried out during the reaction. Initially, only in the monophasic system gave we could

obtain 12 % yield which was very low. However, usingthe different ratio of the DCM-water system with zeolite, the yield obtained was dramatically enhanced [3]. When the proportion ratio reached 1:1, it was observed that the reaction yield was greatest. Further increasing the organic solvent ratio resulted in a decrease in yield. It is interesting to note that the amountof product was reduced when the reaction was carried in pureorganic phase and when the reaction mixture was diluted withaqueous phase the yield was augmented which indicated thatwater is essential for this reaction [3].

Table 3. Optimization of various organic-aqueous solvent systems

Entry No.	Solvent system	Time (min)	Yield (%)	Ratio Organic:Aqueous
1	Toluene-water	60	30	7:3
2	DCM-water	30	45	7:3
3	Cyclohexane-water	70	25	7:3
4	*n*-Hexane-water	66	23	7:3
5	Ethylacetate-water	80	22	7:3
6	DMA-water	75	30	7:3

Table. 4 Optimization of ratio of DCM-water system

S. No.	Organic solvent (DCM) (mL)	Water (mL)	Temp. (°C)	Yield (%)	Time (min)
1	7	4	60	50	45
2	7	5	60	56	42
3	7	6	60	75	40
4	7	7	60	89	30

Table 5. Optimization of catalyst concentrations for synthesis of bipyrimidines (3a-j)

S. No.	Catalyst conc. (mmol %)	Reaction time (min)	Yield (%)
1	10	120	32
2	12.5	115	35
3	16	100	45
4	20	90	47
5	22.5	75	56
6	25	50	87
7	30	30	89

The purity of the compound was confirmed by a single spotin TLC. In IR spectra of compound 2a carbonyl absorption at1722-1690 cm^{-1} and -NH absorption at 3225 cm^{-1} have been observed. The compound showed a mass ion peak of 100 % intensity corresponding to its molecular weight in mass spectrafurther confirming the structure [3]. Furthermore, ^1H NMR spectraof compound 2a, a singlet appeared at δ 2.12 ppm owing to three protons of -CH_3. A doublet at δ 6.93 to δ 6.88 ppm is assigned for one proton of the -CO-CH= group of chalcone with (J = 17.8 Hz). The peak of doublet at δ 7.46 to δ 7.40 ppm represents one proton of =CH-Ar with (J =

17.12 Hz). A singlet for one proton of -NH appears at δ 8.32 ppm and singlet of one proton of -CH of the Biginelli ring corresponds at δ 5.50 ppm. A singlet for one proton of -NH appears at δ 8.23 ppm. The multiplet peaks at δ 7.6 to δ 6.9 corresponds to 10 aromatic protons indicating the presence of two phenyl rings. The product **2a** was analyzed for $C_{20}H_{18}N_2O_2$ which exhibited molecular ion at *m/z* = 318.14 [M+1] [3].

The spectra of the hybrid of synthesized compounds (**3a-j**) wereanalyzed by ^{1}H NMR, IR and mass spectra.The product **3a** was analyzed for $C_{21}H_{21}N_3O$ which exhibitedmolecular ion at *m/z* = 359.17 [M+1] [3].

3.1 Antimicrobial Evaluation

All the synthesized compounds were screened as potent antibacterial and antifungal scaffolds**3a-j**. The microbial study was carried out against two Gram-negative bacterial strains namely *E. coli* (ATCC 25922) and *P. aeruginonasa* (ATCC 8532) and one Gram-positive bacterialstrain named *S. aureus* (ATCC 29213) and against two fungalstrains namely as *C. albicans* (ATCC 10231) and *A. niger* (ATCC 439). The screening was performed with standard drugs such as ampicillin for antibacterial activity and ketoconazole for antifungal activity [3]. The microbial activities of bipyrimidine derivatives were further evaluated for the minimum inhibition concentration (MIC). The inhibitions of microbial growth were used to demonstrate the therapeutic efficacy of hybrid scaffolds. The activity data is illustrated in Tables 6-8. The results of microbial analysis of the tested compounds revealed that thesehybrids have shown moderate to good antibacterial efficacy against selected bacteria strains (*E. coli, P. aeruginosa* and *S.aureus*) [3]. On the basis of the zone of inhibition test against test bacterium, *E. coli*, compounds **3i** (R_1 = Cl, R_3 = OCH_3), **3e** (R_1 = Cl, R_3 = H) and **3f** (R_1 = H, R_3 = Cl) were found to have verygood activity; and compounds **3d** (R_1 = OCH_3, R_3 = OCH_3), **3c**(R_1 = H, R_3 = OCH_3 and **3a** (R_1 = H, R_3 = H) possessed good activity, while compound **3j** (R_1 = Cl, R_3 = OCH_3), **3h** (R_1 = OCH_3, R_3 = NO_2), **3g** (R_1 = NO_2, R_3 = H), **3b** (R_1 = H, R_3 = NO_2) showed moderate activity when compared with the standard drug ampicillin. In the case of *P. aeruginosa*, compounds **3i** and**3f** very good activity and compounds **3a**, **3c**, **3d**, **3e** and **3j** exhibited good activity while compounds **3b**, **3g** and **3h** resulted in moderate activity as compared to the standard drug ampicillin. For *S. aureus*, compounds **3e**, **3f** and **3i** showedvery good activity, compounds **3a**, **3c**, **3d** and **3j** possessed good activity while compounds **3b**, **3g** and **3h** revealed moderate activity in comparison to the standard drug ampicillin [3].

For fungal strains, the screenings of synthesized compounds have revealed very good activity to moderate activity. For *Candida albicans*, compounds **3f** and **3i** showed very goodactivity and compounds **3c** and **3e** possessed good activity while compounds **3a**, **3b**, **3d**, **3g**, **3h** and **3i** exhibited moderate activity as compared to the standard drug ketoconazole. In the case of *A. niger*, compounds **3e** and **3i** revealed very good activity and compounds **3a**, **3c**, **3d**, **3f** and **3g** possessed good activitywhile compounds **3b**, **3h** and **3j** displayed a moderate zoneof inhibition [3].

Table 6. inhibition zones (mm) of synthesized bipyrimidines (3a-j) againstbacteria and fungi by the disk diffusion method

Compound	Microbial							Fungal			
	Escherichia coli (ATCC 25922)			*P. aeruginonas* (ATCC 8532)	*Staphylococcus aureus* (ATCC 29213)			*Candida albicans* (ATCC 10231)		*Aspergillus niger* (ATCC 439)	
	50 µg	25 µg	12.5 µg	100 µg	100 µg	50 µg	25 µg	100 µg	50 µg	100 µg	50 µg
3a	11	12	10	11	12	12	10	10	07	10	07
3b	10	11	09	–	11	09	–	10	08	09	06
3c	12	12	10	12	12	12	10	12	09	11	09
3d	12	11	10	11	13	12	10	11	07	12	09
3e	14	12	10	12	14	14	11	13	09	14	09
3f	14	12	11	13	14	13	11	14	10	15	09
3g	10	11	08	06	10	08	–	11	08	10	05
3h	10	11	09	07	11	10	–	11	07	09	06
3i	15	12	11	13	15	14	12	15	11	15	10
3j	10	10	09	11	12	12	–	11		08	06
Ampicillin	18	15	12	16	32	29	24	–	–	–	–
Ketoconazole	–	–	–	–	–	–	–	20	12	20	12

Table 7. Minimum inhibitory concentrations (μG/ML) of synthesized 3a-J against and Gram-positive and Gram-Negative bacteria

Entry	*Escherichia coli* (ATCC 25922)					*Pseudomonas aeruginonasa* (ATCC 8532)					*Staph yllococcus aureus* ATCC 29213)				
	12.5	25	50	100	App MIC	12.5	25	50	100	App MIC	12.5	25	50	100	App MIC
3a	+	+	++	++	50	–	++	++	++	25	–	+	++	++	50
3b	+	+	+	++	100	–	–	++	++	50	–	+	++	++	50
3c	+	++	++	+++	25	–	++	++	++	25	–	+	++	++	50
3d	+	++	++	++	50	–	++	++	+++	25	–	+	++	++	100
3e	+	++	++	++	25	–	++	++	++	50	–	+	++	++	50
3f	+	++	++	+++	25	–	++	++	+++	25	–	++	++	+++	25
3g	+	+	+	++	100	–	–	+	++	100	–	+	+	++	100
3h	+	+	+	++	100	–	–	+	++	100	–	+	+	++	100
3i	+	++	++	+++	25	–	++	++	+++	25	–	++	++	+++	25
3j	+	+	+	++	100	–	–	+	++	100	–	++	++	+++	25
Ampicillin	+++	+++	+++	+++		+++	+++	+++	+++		+++	+++	+++		

Symbols: (–) Confluent growth (no inhibition), Inactive (< 10 mm); (+) weakly active (07–10 mm); (++) moderately active (11–15 mm); (+++) highly active (16–23 mm)

Table 8. Minimum inhibitory concentrations (µG/ML) of synthesized 3a-J against fungi

Entry	*Candida albicans* ATCC (10231)					*Aspergillus niger*			ATCC (439)	
	12.5	25	50	100	App MIC	12.5	25	50	100	App MIC
3a	–	+	++	++	50	–	+	+	++	100
3b	–	–	++	++	50	–	–	++	++	50
3c	–	++	++	++	25	–	++	++	++	25
3d	–	+	++	++	50	–	–	+	++	100
3e	–	++	++	++	25	–	++	++	++	25
3f	–	++	++	++	25	–	++	++	++	25
3g	–	–	–	++	100	–	–	+	++	100
3h	–	–	+	++	100	–	–	+	++	100
3i	–	++	++	++	25	–	++	++	++	25
3j	–	–	+	++	100	–	–	–	++	100
Ketoconazole	+++	+++	+++	+++		+++	+++	+++	+++	+++

Symbols: (–) Confluent growth (no inhibition), Inactive (< 10 mm); (+) weakly active (07–10 mm); (++) moderately active (11–15 mm); (+++) highly active (16–23 mm)

3.2 Antibacterial Activity

For evaluation of microbial activity, as minimum inhibition concentration of the synthesized compounds was studied at different concentrations as 12.5, 25, 50 and 100 µg/mL. Among these compounds, **3c**, **3e**, **3f** and **3i** exhibitedvery good inhibition at MIC = 25 µg/mL. Compounds 3a and3d showed good activity with MIC = 50 µg/mL and the compounds **3b**, **3g**, **3h** and **3j** revealed moderate activity with MIC = 100 µg/mL against *E. coli [3]*.

Against *P. aeruginonasa*, compounds **3d**, **3f** and **3i** exhibitedvery good inhibition as MIC= 25 µg/mL. Compounds **3b**, **3c**,and **3e** compounds revealed good inhibition with MIC = 50 µg/mL and compounds **3a**, **3g**, **3h** and **3j** resulted MIC = 100 µg/mL. Compounds 3f and 3i exhibited very good inhibitionat MIC = 25 µg/mL, compounds **3a**, 3c and **3e** compounds showedgood activity with MIC = 50 µg/mL and compounds **3b**, **3d**,3g, 3h and **3j** revealed moderate activity with MIC = 100 µg/mL against *S. aureus [3]*.

3.3 Antifungal Activity

Minimum inhibition concentrations of all the derivatives of bipyrimidines for antifungal activity were studied and the results of compounds **3c**, **3e**, **3f** and **3i** exhibit very good inhibition by way of MIC = 25 µg/mL. Compounds **3a**, **3b** and **3d** compounds revealed good inhibition withMIC = 50 µg/mL and compounds **3g**, **3h** and **3j** withmoderate inhibitionMIC = 100 µg/mL against *C. albicans*. In the case of *A. niger* MIC = 25 µg/mL exhibits very good inhibition of compounds **3c**, **3e**, **3f** and **3i**. Compounds 3b showed good inhibitionwith MIC = 50 µg/mL and compounds **3a**, 3d, 3g, 3h and 3j revealed moderate inhibition with MIC = 100 µg/mL [3].

The results depicted in Tables 7 and 8 suggested that theelectron-withdrawing substituents revealed very significant minimum inhibition concentration whereas electron-donating substituents exhibited insignificant minimum inhibition concentration activity against microbial strains [3].

4. CONCLUSION

An expedited process catalyzed by zeolite has the merit of being an environmentally friendly simple operation, involving convenient workup, a short reaction time and resulting in goodto excellent yields. Substituted 2-amino-6-methyl-4,6-diphenyl- 3',4,4',5-tetrahydro-[4,5'-bipyrimidine]-2'(1*H*)-one synthesized by substituted chalcone and guanidine hydrochloride in biphasic system was confirmed by spectral characterization.The synthesized scaffolds of bipyrimidines were studied as anti-microbial agents [3]. The investigation of antimicrobial screeningdata revealed that among 10 compounds screened, compounds3d, 3e, 3f and 3i demonstrated very good activity as comparedto standard drugs and remaining compounds showed good tomoderate inhibition activities.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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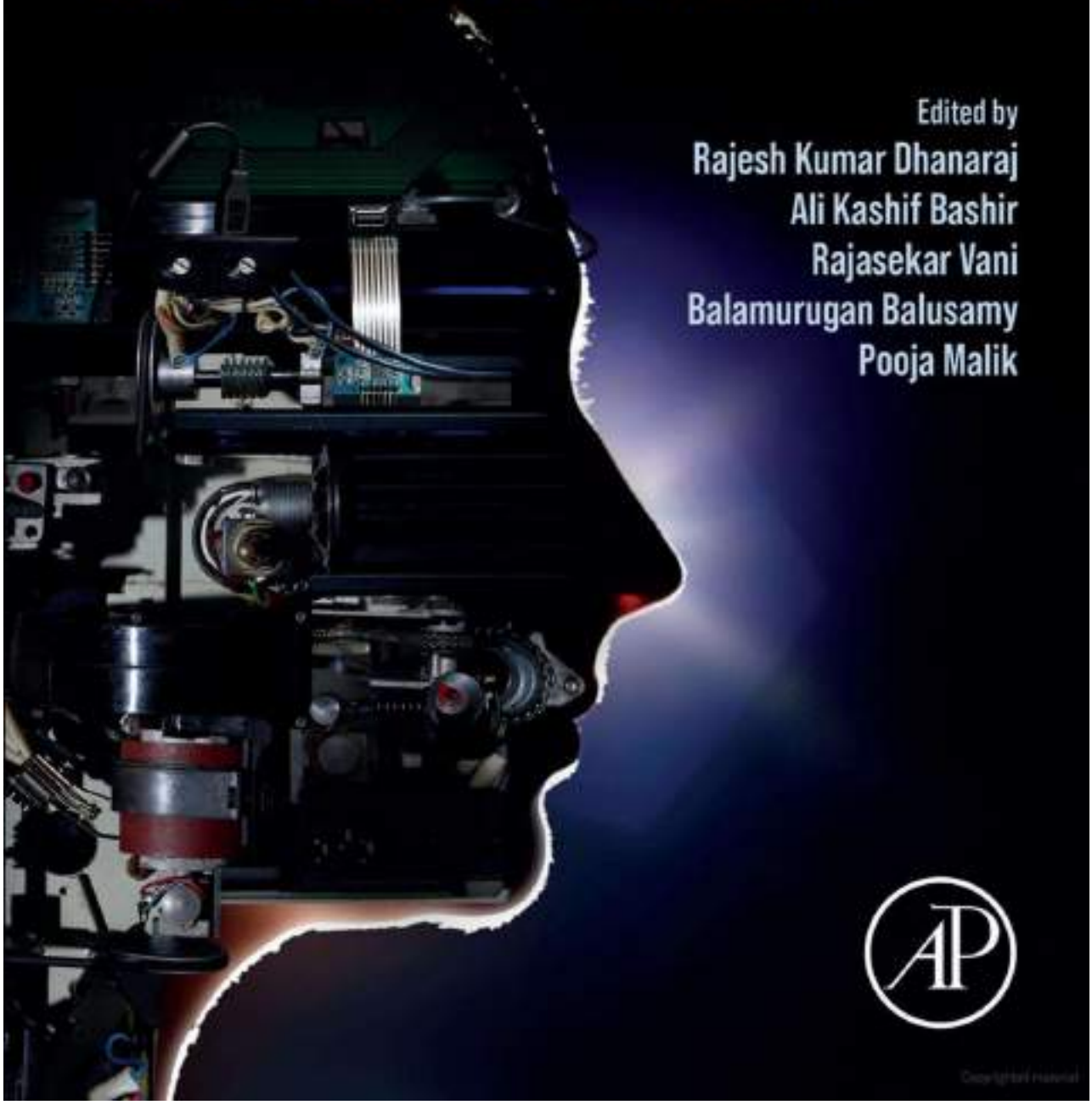

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CHAPTER 7

The convergence of digital twin, Internet of Things, and artificial intelligence: digital smart farming

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7.1 Inroduction

Development of many countries depends heavily on agriculture, which is also essential to achieving Sustainable Development Goal 2 of "Zero Hunger" [1]. To fulfill the demands of a projected population of 10 billion people by 2050, the Food and Agriculture Organization estimates that agricultural output must increase by 40% between 2012 and 2050 [2]. The creative application of technologies like drones, applications, and machines coupled with social, organizational, and institutional shifts is one strategy for enhancing the production.

Around 70% of the freshwater consumed globally is used for agriculture [3]. This makes a strong case for the development of technologies like the Internet of Things (IoT) to increase the amount of food produced on farms while reducing the amount of water required in agriculture.

Irrigation systems utilize the majority of the freshwater that is present, and 40% of the freshwater used in developing nations is wasted due to leakages and over irrigation [4]. The availability of freshwater has become a global concern due to factors including climate change and population growth, specifically due to rainfall.

The regions facing scarcity [5] call for a different viewpoint on irrigation systems and their optimization to guarantee food security for the expanding population [6]. In agriculture, appropriate irrigation that is

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managed by field sensors is crucial, as inadequate or excessive watering reduces crop output [7]. AI can improve the farming process in this context by collecting data on plant conditions and computing it with high performance and low cost [8], maintaining crop yield at normal standards, reducing water waste, and ultimately increasing the availability of potable water [6].

A digital twin model based on the IoT can be applied in farms to effectively recognize their current environment to capitalize on this worldwide concern. This means that a virtual representation of a farm should be able to behave depending on the systems' analyses and judgments as well as gather information from the farm. The fundamental creation of a digital twin for smart farming using the IoT to regulate an irrigation system based on a farmer's and/or AI choice is presented in this chapter. Section 2 of this chapter provides examples of IoT applications in agriculture, Section 3 introduces the idea of a digital twin in the context of agriculture, Section 4 details the creation of the digital twin, Section 5 describes the initial findings and analysis, and Section 6 concludes the chapter.

7.2 Internet of Things in agriculture

The majority of the literature on the development of IoT technologies in agriculture consists of exploratory research that demonstrate systems in small pilot projects [9]. The development of equipment and devices used on farms to gather information about the soil, crop quality, weather conditions, and other factors can be divided into two categories when it comes to the use of IoT in agriculture [10,11]. The second category includes the development of platforms that are used to store, organize, analyze, and visualize data to help in the decision-making [12,13].

The term "smart farming" appears while reading the literature on the application of information and communication technologies (ICT) in agriculture. Although the term "smart farming" has been in use for some time, there is still a need for a comprehensive definition of the term that encompasses the technology now employed in the agriculture industry. To integrate information and communication technologies in the cyber-physical farm management cycle, smart farming entails integrating them into machinery, equipment, and sensors [14,15].

Several technologies, including IoT, big data, AI, process management, etc., are perceived as being included in this notion. According to the

literature, ICT usage in agriculture is a developing field that currently faces some challenges, but there are also many advantages associated with its use.

7.3 Digital twin smart farming

According to the research by [16], a digital twin model is one in which allows data transfer between a physical and digital entity automatically, as seen in Fig. 7.1. By utilizing technologies like big data, IoT, AI, etc., a digital twin is able to link information about the farm and business and is able to act depending on a choice made automatically by the system.

By extending the idea of smart farming, a digital twin for a smart farm or a digital smart farm is suggested. Building discrete services to understand the data of a specific system, such as an irrigation system, a seeding system, etc., and bringing them together in a cyberphysical system is how a digital smart farm is executed. This makes it possible to combine various systems and gives farmers a thorough understanding of how their crops are doing. It is possible to adjust the farm to changes in the environment, weather, markets, water limitations, etc., by employing a digital smart farm.

7.4 Digital smart farming system

This section, which is separated as follows, describes a digital smart farm based on two initiatives (The Sensing Change and SWAMP projects): The previous two projects are summarized in Section A, the system design

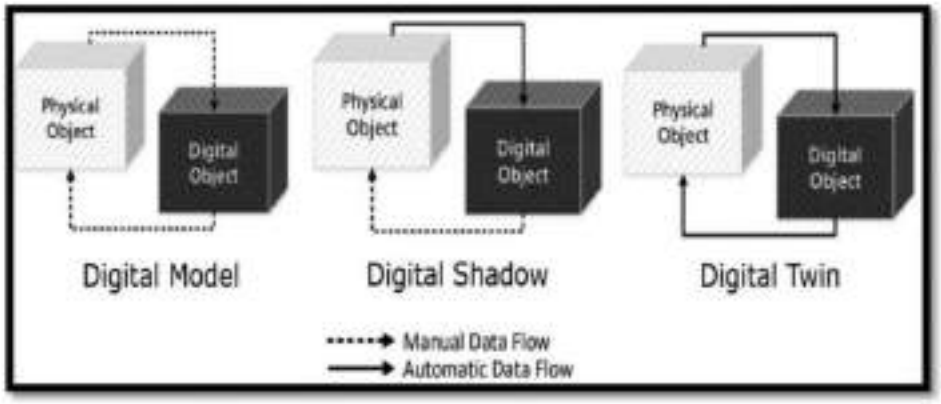

Figure 7.1 Digital twin concept [16].

is described in Section B together with its hardware and devices, and the system architecture is shown in Section C along with cloud services and other components.

7.4.1 Sensing change and smart water management platform programmers are related works

The Sensing Change project's approach was based on the idea that it could be applied to any type of agricultural activity and that it could make use of low-cost commercial tools and supplies [17]. Three key parts make up the system: the monitoring station, the smartphone app, and the cloud system (Fig. 7.2). This project created an information-gathering and information-analysis monitoring system for a farm. However, it was the farmers who made the decisions and took the necessary steps.

The SWAMP project, on the other hand, is creating a hands-on, IoT-based smart water management platform for precision irrigation in four locations across Brazil, Italy, and Spain [18]. The SWAMP platform can be designed and implemented in various ways, resulting in several SWAMP systems that are tailored to meet the needs and limitations of various settings, countries, climates, soils, and crops. This indicates that the decision-making process can be entirely handled by the farmer, by a machine, or by a combination of the two. According to Fig. 7.3, the SWAMP design is separated into five layers.

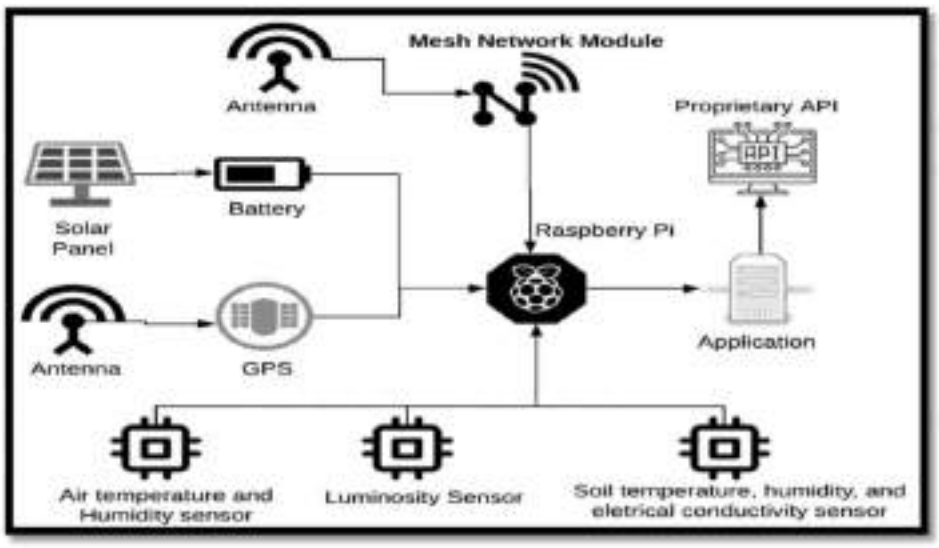

Figure 7.2 Sensing change system diagram [17].

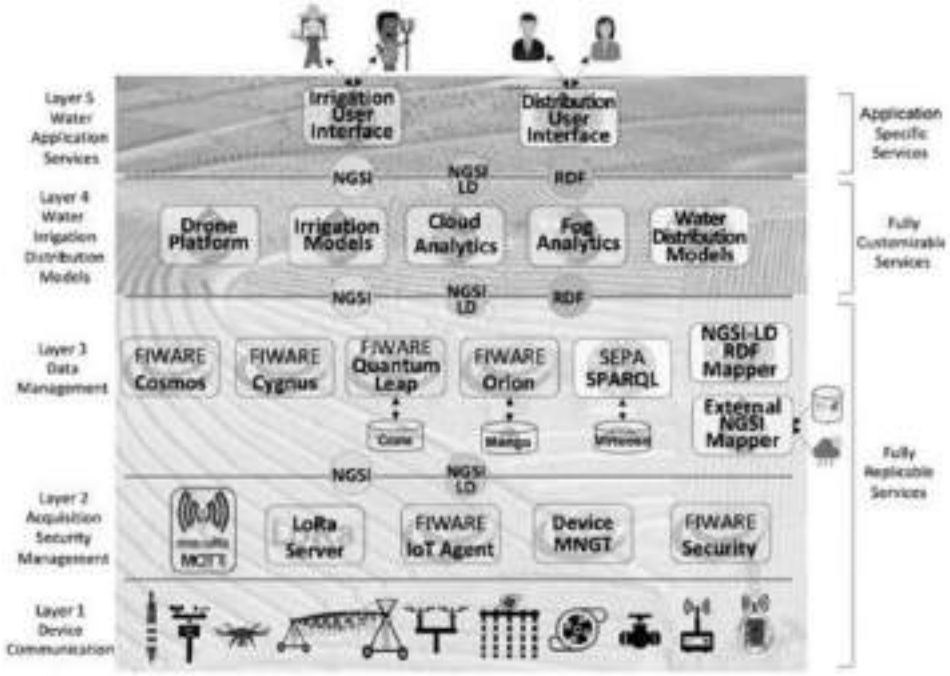

Figure 7.3 Smart water management platform project architecture layers.

7.4.2 A system design

The system comprises a field-installed probe that measures ground temperature at 7 cm depth (DS18B20), soil moisture at depths of 7, 28, 50, and 72 cm, ambient light, and geographical position (CSMv1.2). The Raspberry Pi-3 module receives probe signals via the I2C bus (CSM v1.2 and BH1750), GPIO (DHT22), serial bus (Venus GPS), and One-Wire bus (DS18B20). a module for ADS1115 is also employed for the conversion of the CSMv1.2A/D signal. This data is read by the Raspberry module using a Python script, which displays numbers as percentages of soil moisture. The script then generates a payload including all probe data and delivers it to the Orion broker for subscription via the IoT agent. A prototype of the system utilized for laboratory testing is shown in Fig. 7.4. The final model of the probe that can be seen in the figure will be used in the field.

7.4.3 System architecture

Numerous equipment and systems, such as soil probes, weather stations, irrigation systems, seeders, harvesters, etc., are used on the farm. These tools and equipment are linked to the cloud through a gateway, which

Figure 7.4 System design.

communicates data to an IoT agent. The suggested system architecture is shown in Fig. 7.5, along with the services employed.

1. A service called Fiware IoT Agent converts many communication protocols to the cloud-based standard.
2. The term "fiware" Orion is a context broker that enables you to control every stage of the context information lifecycle, including updates, queries, registrations, and subscriptions.
3. A document-based database called Mongo DB is used to store the most recent data in a complex structure.
4. Draco is a generic enabler that is a different data persistence method for controlling context history.
5. Time-series data are kept in MySQL, an open-source relational database management system.
6. MySQL Grafana is an open-source analytics and monitoring tool for building data dashboards.

This digital environment is intended to visually enlighten the data gathered by IoT and to deliver data to the systems based on the decision-making

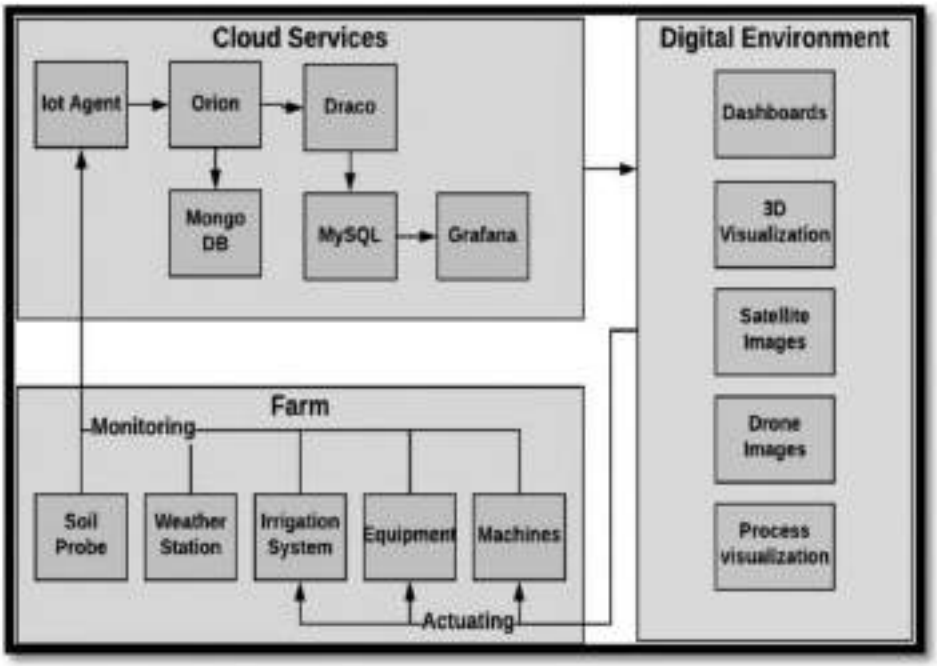

Figure 7.5 System architecture.

process carried out inside of it. Information can only currently be displayed visually on dashboards.

However, all of the other settings must be built in an integrated manner to properly construct the digital smart farm. The information gathered and analyzed in the cloud and represented digitally should be entered into the physical system via the cloud or by integrating programmable logic controllers into the machinery, equipment, and irrigation system.

7.5 First result and analysis

The system's initial testbed findings are shown in Fig. 7.6 in our laboratory. On the basis of the thermogavimetric data, the soil moisture sensor was calibrated [19]. This initial test shows that the probe can send data to the cloud and that it is possible to display that data in a dashboard that updates in real time. It is obvious that the air temperature and humidity have dropped abnormally, which suggests a hardware or communication issue that has to be further investigated.

Fig. 7.7 displays field data that was gathered using a nearby weather station. The Penman-Monteith equation can be used to extract the

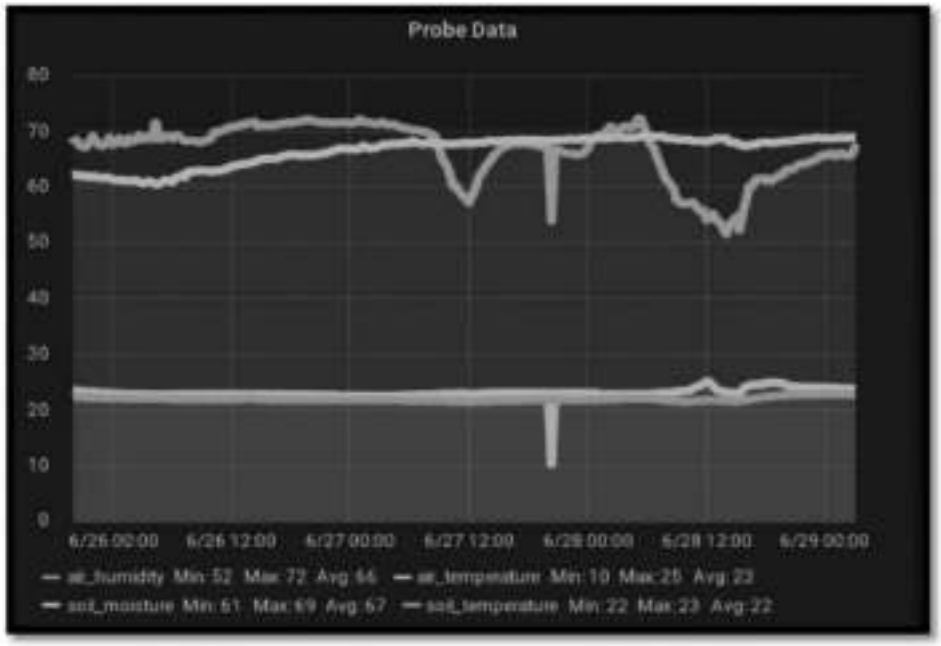

Figure 7.6 Dashboard with probe data.

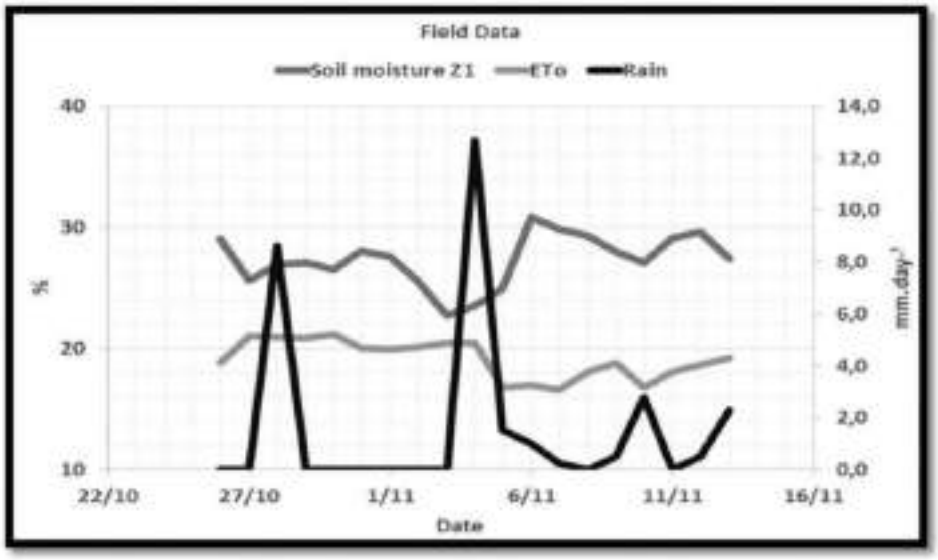

Figure 7.7 Field data collected.

reference evapotranspiration (ETo) using data from this meteorological station, including air temperature and humidity, wind velocity and direction, rainfall solar radiation, dew point, rain forecast, and rain chance [20].

The crop evapotranspiration is calculated by multiplying the ETo by the crop factor (Kc) for the specified crop. The ETo stands for the amount of water, in millimeter, that the reference crop uses [21].

The initial findings show that the technology is functional and capable of uploading data to the cloud for usage in spreadsheets and dashboards. Additionally, it is possible to display the water patterns in the soil and extract ETo using the nearby weather station. It is clear from Fig. 7.7 that during periods of drought, the soil moisture reduces and increases after each rainfall.

7.6 Conclusion

Farmers can connect various assets and systems utilizing the digital twin concept and IoT technology to have a better understanding of the various factors and elements that affect the farm's behavior, final yield production, and resource use. This essential component helps farmers make wiser decisions and minimize their influence on the environment's water, land, and soil resources. This chapter outlines the preliminary steps in creating a digital smart farm. However, numerous systems must work together to represent all of the farm's functions before a digital smart farm can be fully implemented.

According to this study, system architecture and cloud implementation are effective and may be utilized in the deployment of the subsequent steps, which include the creation of AI algorithms and other digital contexts. Once the complete system is operational, it will be feasible to comprehend how farms use resources and how that affects agricultural productivity. This promotes sustainable development and enhances food security for everyone on the planet.

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PREFACE

In the ever-evolving landscape of science and technology, knowledge is a beacon that illuminates the path to progress. The pursuit of understanding and innovation has been the driving force behind the remarkable advancements that have shaped the world we live in today. As we embark on a new era, it becomes increasingly crucial to navigate through the diverse and dynamic currents of research to discern the trends that will define our future.

"Research Trends in Science and Technology" represents a collective effort to explore and elucidate the cutting-edge developments that are shaping the fields of science and technology. This book is an assembly of insightful chapters contributed by leading experts, researchers, and visionaries, all of whom share a common passion for unraveling the mysteries of the universe and harnessing the power of technology for the betterment of humanity.

In this volume, we delve into a broad spectrum of disciplines, ranging from fundamental sciences such as physics, chemistry, and biology to the transformative fields of artificial intelligence, nanotechnology, and biotechnology. By curating a diverse selection of research trends, we aim to showcase the interdisciplinary nature of modern scientific inquiry and the interconnectedness of technological breakthroughs.

We believe that knowledge should be shared and disseminated freely, fostering a collaborative spirit that transcends geographical and disciplinary boundaries. As such, "Research Trends in Science and Technology" serves as a platform for disseminating the latest discoveries, ideas, and perspectives that shape the course of human progress.

We extend our heartfelt gratitude to all the contributors who have dedicated their expertise and passion to enrich this compilation. Their invaluable insights and visionary outlooks have made this endeavor possible.

We hope that this book will inspire readers, whether they are students, researchers, policymakers, or curious minds, to embrace the spirit of inquiry and embark on their own explorations. By staying attuned to the latest research trends and leveraging collective knowledge, we can collectively chart a course towards a more sustainable, equitable, and innovative future.

Editors

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Research Trends in Science and Technology Volume III
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A REVIEW OF THE INTERPRETATION OF DUALITY IN DIFFERENTIABLE AND NON-DIFFERENTIABLE MATHEMATICAL PROGRAMMING

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Abstract:

The existence of an ideal solution to either the primal problem or the dual problem ensures the existence of an ideal solution to the other because these two projects are linked by the duality principle. If the primary issue is constrained minimization (or maximisation), then the dual issue is a constrained maximisation (or minimization) problem. The duality effects have shown to be very helpful in enhancing numerical techniques for addressing particular categories of optimisation problems. Because it offers appropriate halting guidelines for primary and secondary problems, The presence of duality theory in nonlinear programming problems makes it easier to create numerical algorithms. The inclusion of duality theory in nonlinear programming issues aids in the development of numerical algorithms. If the original issue is the dual of the dual, then a nonlinear programming problem and its dual are said to be symmetric. This postulation's major objective is to take into account optimality and duality in a range of mathematical programming issues, with a particular emphasis on non-differentiable nonlinear programming and variational issues, such as blended sort symmetric and self duality. Non-differentiable fractional minmax programming, continuous-time minmax programming, minimaxvariational problems, and continuous-time minmax programming.

Overview

In the late 1940s, mathematical programming achieved the status of a logical science unto itself, and ever since then, it has made enormous strides. It is currently regarded as one of the most dynamic and invigorating disciplines of contemporary mathematics, with numerous applications in a variety of contexts, including design, financial matters, and basic sciences. Mathematical programming problems frequently include finding the least-weight design of a structure that is bound to stress and deflection restrictions.

A mathematical programming problem has the following structure:

(MP): Maximize or minimize $f(x)$.

Depending on

$g_i(x) \leq 0, i = 1,2,3 \ldots \ldots, m$

$h_j(x) = 0, j = 1,2,3 \ldots \ldots, k,$

$x \in$ X

The function f and each of its f_j and h_j on the n-dimensional Euclidean space R_n and XR_n are real valued capabilities. This is referred to as the general mathematical programming issue. Fairness constraints are defined as $h_j(x) = 0, j = 1,2,3 \ldots \ldots, k,$ whereas inequality constraints are defined as $g_i(x) = 0, i = 1,2,3 \ldots \ldots, m.$The integration of x X is a conceptual constraint. We define the previous issue as a differentiable programme if the objective and critical skills are differentiable. The aforementioned issue is referred to as a convex programming problem if X is a convex set and the objective and inequality constraints are both relative to capacity.

Duality in adaptable mathematical programming

If f: Rn R and hj: Rn R, where j = 1, 2,..., m, then think about the nonlinear programming problem:

Min $f(x)$(P) according to, $h_j(x) = 0, j = 1,2,3 \ldots \ldots m.$

The Lagrangian dual for issue (P) in the case of Rm is defined as

This is,M inf (u) plus $Th(u)$ (LD)

If all of the functions f and $h_j(x) = 0, j = 1,2,3 \ldots \ldots m.$ are differentiable convex functions, then the problem (LD) is similar to the problem below:

$Maxf(x)+ Th(x)$ (WD)

Depending on $Vf(x)$ plus $Th(x)$ = 0, 0 and R_m,The Wolfe type of dual for the issue (P) is superior than everything else here. When Mangasaria gives an example, he suggests that some duality theorems might not hold true if the goal function or the constraint function is a summed up convex function. This inspired Mond and Weir to create a new dual for (P) as a result.

$Maxf(x)+$ (MWD)

Depending on

$f(x)+ + \lambda\, Th(x) = 0, \lambda\, Th(x) \geq 0, \lambda \geq 0, \lambda \in R_m,$

Non-differentiable mathematical programming duality

The class of non-differentiable mathematical programming issues that Mond took into account was as follows:

Min f(x) + xTBx 1/2 (NP)

depending on $h_j(x) \leq 0, j = 1,2,3 \ldots \ldots m.$

In this case, B is a n X n positive semi definite (symmetric) matrix, and f and $h_j(x), j = 1,2,3 \ldots \ldots m.$ are twice differentiable functions from Rn to R. The functions f and hj (j = l, 2,...,

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m) are anticipated to be convex functions. They established a duality theorem between (NP) and the following problem.

(ND): $[f(u) + y\,Th(u)]\ \ maxf(u) + y\,Th(u)] - uT$

according to,

$yT + f(u) + h(u) + Bw = 0, wTBw\ 1, y \geq 0.$

A new dual program was introduced by Chandra, Craven, and Mond along the lines of Mond and Weir:

$Maxf(u) - [uTf(u) + yTh(u)]$ (NWD)

depending on $Bw = f(u) + yTh(u)$

$yTh(u) \geq 0, wTBw \leq 1$,y$\geq 0.$

Additionally, for any possible solution to (NP) and (NWD), settled duality theorems by assuming that $f(u)$ + $wTBw$ is pseudoconvex and that yTh is quasiconvex.

Later, Mond and Schechter replaced the square root term with the standard term and, in addition, defined the non-diffemtiable nonlinear programming problems as follows:

(NP)1 Min ||Sx||p $+f(x)$

according to, $h_j(x) \leq 0, j = 1,2,3 \ldots\ldots.m.$

Here, the convex functions f and h_j $(j = 1,2,3 \ldots\ldots.m)$ are twice differentiable from Rn to R. The problem is the dual for (NP)1:

$Maxf(u) +$ [$yTh(u)$+ uTS Tv (NP)

according to $F(u) + Y\,Th(u) = \|v\|, q \leq 1, y \geq 0.$

where conjugate instances for p and q are.

Symmetric duality in distinctive mathematical programming

Take a look at a capacity f(x, y) that can be differentiated in the ranges Rn and Rm. The challenges that Dantzig et al. introduced are as follows:

$Min(f(x,y) - yTy\ f(x,y)$ (SP)

Depending on

$yf(x,y) \leq 0$,$(x,y) \geq 0. Maxf(x,y) - x\,Tf(x,y)$ (SD)

Depending on $Vxf(x,y) > 0, (x,y) > 0.$

Additionally, the existence of a typical optimal solution to the primal (SP) and (SD) was shown when (i) f is convex in x for every y and concave in y for every x, and (ii) f, which is twice differentiable, has the property that its matrix of second partials for y is negative definite at (x_0, y_0) and also provided the information below regarding symmetric dual programming issues:

$Min(f(x,y)$ (MSP) $yTy\ f(x,y)$

depending on $f(x,y) \leq 0, x \leq 0.\ Maxf(x,y)(MSD)x\,Tf(x,y)$

depending on $xf(x,y) \geq 0, y \geq 0.$

It should be noted that whereas in both (SP) and (SD) the constraints include x 0 and y 0, only x 0 is necessary in the primal and only y 0 is necessary in the dual.

Hypothetical duality in non-differentiable mathematical programming

Suppose $f(x, y) =$be a true esteemed continuously differentiable function in the intervals x Rn and y Rn. Chandra and Husain created the following set of symmetric dual non-differentiable algorithms to demonstrate how duality is a result of the convexity-concavity assumption applied for the bit function $f(x, y) =$:

$Min(f(x, y) = yTyf(x, y) + (xTBx)_{1/2}$

depending on Cw −yf(x,y) ≤ 0,wTCw ≤ 1,(x,y) > 0.

$Maxf(x, y) - x$Tx, $f(x, y)$- (yT Cy)1/2 (ND)

depending on $f(x, y)$ − Bz ≤ 0, zTB z ≤ 1,$(x, y) \geq 0$.

n x m and m x m positive semi-definite matrices, respectively, make up B and C.

Chandra, Craven, and Mond showed another combination of symmetric dual non-differentiable algorithms by reducing the convexity criteria on the bit function f(x,y) to pseudoconvexity.

The issues in are as follows:

$Min\ f(x, y)$+ (xTBx)1/2−yTCz (PS)

depending on Cz = yf(x,y) = 0.When yT[y f(x,y) - Cz] > 0,zTCz ≤ 1,x ≥ 0 .

Max $f(x, y)$ − (yT Cy)1/2 + xTBw (DS)

depending on Bw + $xf(x, y) \leq 0$, If xT[$xf(x, y)$+ B w] is zero, wTB w ≤ 1,y ≥ 0.

Programming with differentiable fractions

Assume that $f, -g$ and h_j (J = 1, 2, and m) are real, esteemed, differentiable convex functions defined on the open convex set X Rn. Consider the convex-concave fractional programming issue at this point. (FP): Depending on

h_j ≤ 0, (j = 1,2,…,m)

S = x X:hj (x) 0; j = 1, 2,..., m; g(x) > 0 for every x X; and if g(x) is not

Affine, then for all x X, f(x) ≤ 0.

There are two prominent duality models for (FP), and these have been extensively discussed in the work. These are a result of Schaible, Jagannathgan, and Bector. The issue is the Bector's double [17] for (FP).

according to,

The accompanying proportionate problem (EPF) of FP is essentially represented by this Wolfe double:

EFP: Minimum according to,

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In (BD), one needs that $f(u) + yTh(u) \geq 0$, if g isn't relative, in order to make the target function pseudoconvex and ensure that duality theorems are true.

Programming that is not differentiable in fractions

Mond thought about the following fundamental issue according to,

$h(x) \leq 0.$,

In this scenario, G(x) > 0 for every possible x, B and D are n x n symmetric positive semidefinite frameworks, f, g, and h are differentiable functions from Rn into R, Rm separately. Mond [9] developed suitable duality theorems under convexity assumptions on f, g, and h, described a twofold problem to the (NFP) issue, and proved necessary and sufficient conditions for the existence of an ideal solution.

After some time, Zhang and Mend found a number of conditions that had to exist in order for the optimal configuration of (NFP) to exist. Additionally, as an application of these optimality requirements, the first and second request duals indicated below were derived individually, and relevant duality theorems were also produced.

Diverse problems

A variation problem is a particular example of an optimum control problem where the state function is subordinate to the control function.

In terms of numbers, the following variational problem exists:

Depending on

The separation operator D is given by $y = \text{Dx} \Rightarrow x(t) = x(a) + (s)ds$ except at discontinuities, and C (I, Rn) is the space of persistently differentiable functions x: I Rn. Where f:I x Ru x R n Rm and g:I x Ru x Rn Rm are persistently differentiable functions as for each of their contentions. Valentine establishes the necessary circumstances for the presence of an external force (VP).

Final summary

But in the current context, the heightened competitiveness and customer expectations frequently require the greatest solutions, not just practical ones. It has been found that even shortening the time it takes to improve can help a corporation save money by enhancing the design process. In this manner, the optimisation theory regulates selecting the best option among a few alternatives in terms of given capacity with the minimum amount of resources that is theoretically feasible. Mathematical programming problems are a new class of problems as a result. The most effective approaches for solving problems are frequently applied in operations research and are known as mathematical programming techniques.

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Study the Flow of a Newtonian Fluid in a Cylinder with a Peripheral Layer Using Numerical Methods

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ABSTRACT

Peristaltic flows are beneficial for resolving problems with physiological flows. In order to represent a variety of fluid motions involving peristaltic, a number of problems involving distinct fluid behavior assumptions and geometrical configurations have been solved. This work considers the passage of a Newtonian fluid through a cylindrical tube in the presence of a peripheral layer of a Newtonian fluid with a different viscosity. It is determined what the relationship between flow rate and pressure difference is. In this paper, the trapping and reflux limits, as well as the pumping efficiency, are determined. The problem is analyzed numerically, and the results for peripheral layer viscosity, pressure difference, and pumping efficiency are obtained.

Keywords: Blood Flow, Artery, Arteriosclerosis

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Exploring the Reliability of the System in Various Configurations with Different Components

Nikhil Vikas Jaipurkar[1*] and Dr. Ram Naresh B. S. Sisodiya[2]

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ABSTRACT

Our study is a comprehensive exploration of complex system reliability across various configurations, encompassing diverse sets of components. We sought to gauge the dependability of these systems, an essential facet in industries, infrastructure, and technology, where real-world conditions and configurations vary. Our approach involved meticulous analysis, breaking down the systems into their constituent components. We calculated individual reliabilities for components operating in both series and parallel configurations. This dual focus allows us to understand the critical interplay between component reliability and system design. In series, each component is vital; in parallel, redundancy offers a safety net. The paramount goal was to establish a benchmark for evaluating system reliability in diverse real-world scenarios, enabling engineers and designers to make informed decisions about system configuration and maintenance. We presented our findings graphically, providing a clear, comparative view of system reliability across different setups. In summary, our research contributes to the foundational understanding of complex system reliability, furnishing valuable insights for industries, infrastructure, and technology. By creating a visual roadmap for system performance under varying conditions, we equip decision-makers with the tools to build more dependable, resilient, and robust systems in an ever-evolving technological landscape.

Keywords: Reliability, Failure Rate, Reliability Block Diagram

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Present Status of Women in India

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Introduction

In modern times, however, due to the low social, economic and political status of women and increased oppression of women, the condition of women who are considered goddesses has become very miserable. According to law, women have got rights and position equal to men. The new system gave equal rights to women. Despite much talk of women's participation, equality has not been achieved in reality.

Even though our constitution has advocated the principle of equality between men and women, the position of women in the society has always remained secondary compared to men. Therefore, male dominance is found in all fields in our society. Even in daily life, women get secondary treatment from men. Father's words are more important than mother's. A brother's life is considered more than a sister's. The husband enjoys more freedom than the wife. A common experience like this reveals the secondary position of women. Earlier there was a society where a woman could not do the work or role that a man does. Because women are weaker than men. But women are not weaker than us men in our abilities. This has been proven. Women are now doing jobs that used to be monopoly of men. There are also women in the police and army. Women are working shoulder with men in all fields. Today there is no sector in which women are not working. Be it politics or social causes, women are at the forefront in all fields. Every educated parent wants their daughter to get higher education and get a job. While getting married, every boy thinks that he should get a working wife. So much change is seen in people's thinking today.

Education and employment changed the family roles of women is Men in families where women are employed help their wives in housework do Earlier men did not help their wives in housework, by the husband doing housework was considered inappropriate. But in the mindset of men Parivarman has happened. Therefore, there is a change in the traditional role of women. As women are inferior their status is inferior to men. Come on there has been a change in the traditional thinking of man. Women with their skill the quality has changed. While studying the current status of women in India in ancient times it is necessary to think about

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the role and status of women. Because many of today's problem can be traced back to historical times of women in India

After independence, special efforts have been made in terms of law to give equal status to women in Indian society. The Constitution of India Provides equal rights to both men and women without any distinction. So women are not inferior to men. They too can play any role as well as men. They just have to get a chance. The idea that women should not be underestimated gradually started to take root in the Indian society.

The human values of liberty, equality, fraternity and justice began to influence the generation born after independence. Therefore, giving education to girls like boys, giving them jobs, and not distinguishing between men and women became very important. People started educating their daughters. Educated women started working. Therefore, the traditional role and status of women began to change.

Today a women in not limited to 'Chul and Child' only. Earlier in Indian society, men and women were assigned different roles based on gender. Women should stay at home and do all the household chores. Her roles were to give birth and bring up children, to serve the people of the family, etc. The woman was not making money. Only the women of the lower classes were engaged in agricultural work and mercenary work. Overall the roles of women were traditional. But these roles of women have changed a lot in modern times. Like boys, girls have also started working with higher education. Education, employment and new responsibilities have changed the traditional roles of women. It is found that the proportion of working women is gradually increasing.

To study from a historical perspective, different eras have been categorized on historical basis. The status of women at that particular time.

1.**Period of Indus Civilization (2000 to 1750 BC) :** The history of India is ancient many thinks explained that the Indus civilization had a matriarchal family system. Tartaktirtha Lakhmanasastri joshi clearly mentioned in his book Vikas Vedic Sanskriti that before the time of Rigveda there was a matriarchal family system in India. The region from the Indus to the Nile was once under a matriarchal family system of society. This conclusion was presented by Marthal. Excavations at Mohanjodoro and Harappa have found numerous female figurines of red and soft stone with images of the seven matrikas carved in rows on a shiki. Therefore, it can be inferred that mother worship was performed in Indus culture women had an important role in the family and society and their status was good. "The idea of woman as the primordial nature of creation did not strike a chord in Dravidian culture."

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Conclusion:

If present times the status of women has been raised. The status of women has increased in various fields such as social job, political etc. Not only this, women have now got a position equal to men in the family as well from this it is clear that in present times the role and status of Indian women is equal to that of men . Now their status has not deteriorated as before.

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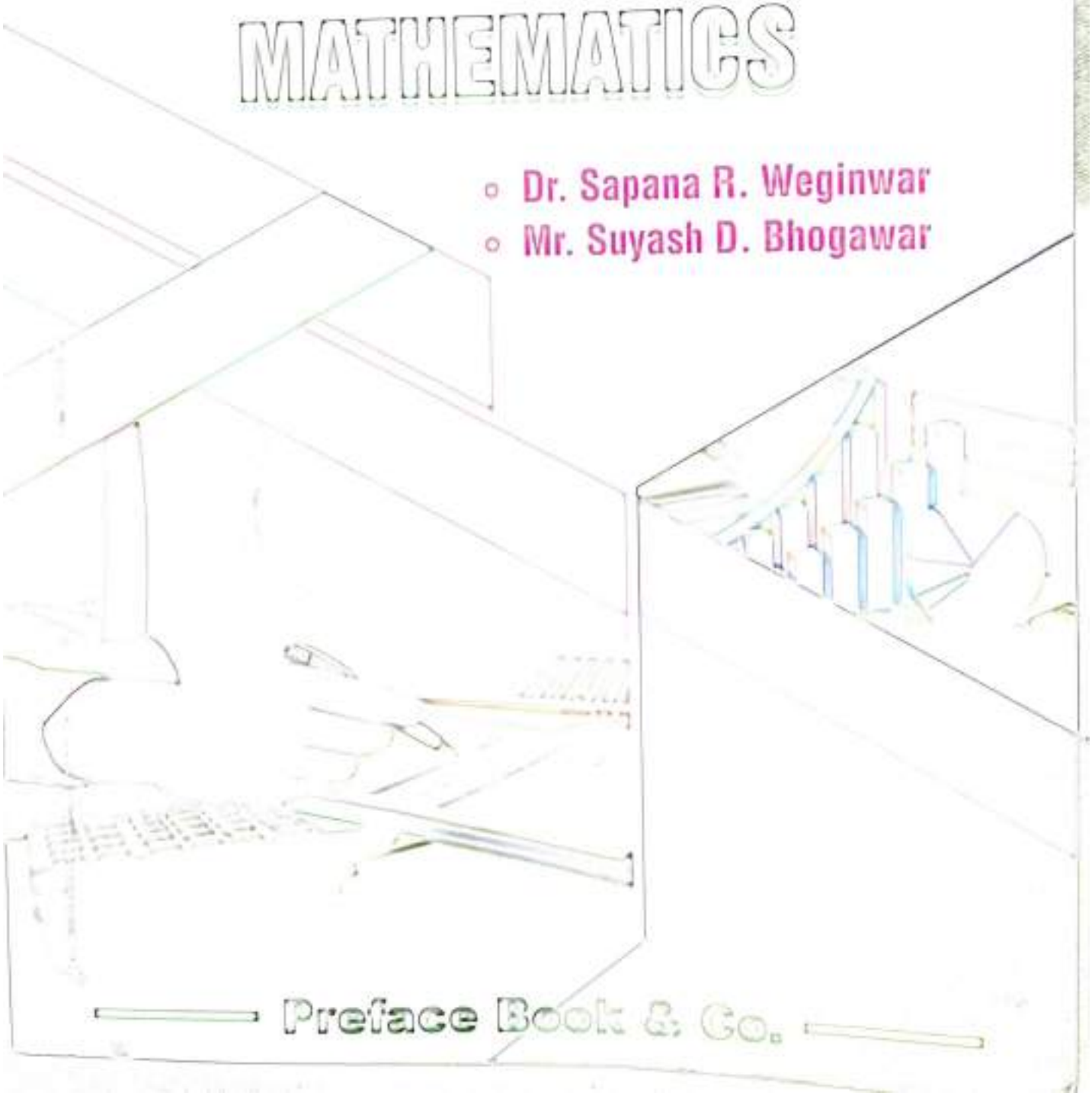

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Preface

We take immense pleasure in presenting the Book statistical Techniques and Business Mathematics to the readers at Gondwana University, Gadchiroli.

This book aims to fulfill the comprehensive needs of students preparing for B.Com. I semester - I. It includes numerous solved illustrations from various university examination. Additionally, each chapter provides a sufficient number of unsolved problemsfor self-practice. Gradtitude extends to my spous, wards, parents, friends and relatives for their support. Special Thanks to our publisher M/s Preface Book & Co., Nagpur for printing the swift printing of this excellent publication. Any suggestions for improvement in this book are most welcome.

30th October 2023

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Holding M.Com, M.Phil., and Ph.D. degrees in Commerce and Management, currently serves as an Associate Professor at Sardar Patel College Chandrapur since 2007. With 17 years of dedicated teaching experience in Commerce and M.A. Economics, she has authored 10 books spanning subjects like cost accounting and statistics. Dr. Weginwar is not only a registered Ph.D. guide but also contributes to Gondwana University Gadchiroli as a Board of Studies member. Her extensive research includes numerous papers presented in national and international conferences, along with publications in reputable journals. Recognition of her scholarly work includes two prestigious awards from a renowned society. Quite an accomplished journey

Mr. Suyash D. Bhogawar

A holder of a Bachelors of Engineering and Masters of Science from the USA. Currently, I serve as a Data Science Architect at RACKSPACE TECHNOLOGIES California USA, specializing in healthcare, neuroscience, and medical informatics.In my role as a research engineer, I've led and contributed to various data science and AI projects, driven by a passion for the foundational principles of statistics. Beyond work, I am a lifelong learner, staying updated on the latest developments in engineering, healthcare, economics, and data science. I believe the convergence of these fields holds the key to driving impactful innovations for an improved quality of life.Thank you for taking the time to learn more about me. I look forward to continuing my journey of positive impact in Statistics and Informatics, contributing to the advancement of knowledge in these dynamic fields

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Advancement in Functional Materials

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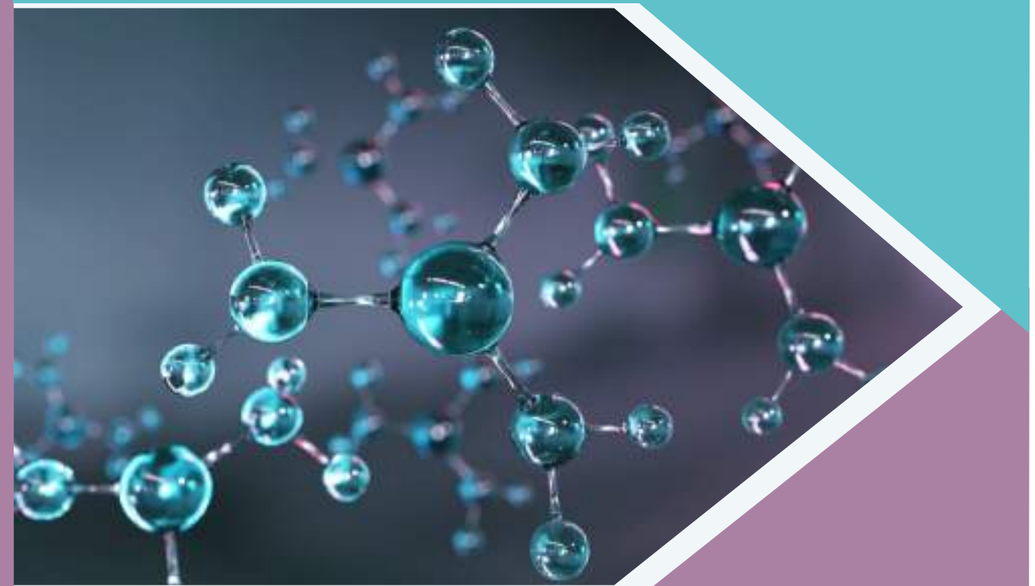

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27 ILLUMINATION OF MECHANICAL, THERMAL AND ELASTIC PROPERTIES OF TRIPLE SUPER PHOSPHATE (TSP) IN AQUEOUS MEDIA: AN ULTRASONIC TACTIC

Paritosh L. Mishra*[1] ***and Urvashi P. Manik***[2]

ABSTRACT

The ultrasonic tactic/approach helps to quantity the speed of sound in pure as well as in different liquids mixture. By obtaining these experimental data of speed of sound and density, various properties (like, mechanical, thermal and elastic) of the liquid and their mixtures can be calculated. These properties are too useful in understating and gathering the knowledge of interaction between the solute and solvent components of liquid and their mixtures. In view from this scenario, present manuscript reports the investigation of TSP in aqueous media to explore the intermolecular interaction in the liquid system (TSP+H_2O) at fixed 2MHz frequency by varying the concentration and temperature. All mechanical, thermal and elastic parameter shows the positive values suggesting strong intermolecular interaction among ions of solute (TSP) and solvent (H_2O/NaCl/Na_2SO_4) through hydrogen bonding. This kind of data provides the information requires in many aspects and have applications in the field of agriculture sectors through which the quality of fertilizer (TSP) can be improved.

Keywords: Acoustic, elastic property, mechanical property, thermal property, ultrasonic

INTRODUCTION

The excess concentration of salts in agricultural land not only generates the problem of salinity but adverse effects in plants and possess risks to human health.[1] Due to this rapid salinization, the scarcity and limited food resources, have created burden and pressure for the survival of human needs unless certain measures are taken to, overcome this pressure. To achieve food security, the attempts need to focus on both area expansion under agriculture as well as a rise in crop productivity.[2]

Accordingly, it is needed to develop a simple and low-cost method for soil salinity management to enhance the productivity of crops to meet the ever-increasing requirement of food also to improve the high and regular income and employment generation to the farmers.

In view to resolve these problems, fertilizers are applied in agricultural

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land worldwide to supply the micro and macronutrients for bulk crop production, to provide better plant nutrition, and to increase the fertility of saline soil.[3] Literature survey revealed that the efficiency of fertilizer is higher than salt affected soil as compared to non-saline salts. The capacity in the absorption of P type macronutrient may be decreased in existence of surplus Cl or SO_4. However, P type macronutrients not only fulfill their deficiency in soil but also reduce their adverse effects like Cl or SO_4.[4]

As ultrasonic is a versatile non-destructive technique and highly useful for investigation of various physicochemical and thermo-acoustical properties of pure liquid as well as liquid compositions.[5,6] Recent developments have found the use of the ultrasonic technique in medicine, engineering, and also in the agriculture field. Thus, this kind of study is important for both human beings as well as plants. Because of the above circumstance, an effort was carried out to fulfill the stated circumstances and to bring out such studies on fertilizer: Triple Super Phosphate of different concentrations viz. 0.002–0.02 $mol.kg^{-1}$ change by weight fraction in water and aqueous 0.2 $mol.kg^{-1}$ solutions of salts namely: Sodium Chloride and Sodium Sulfate at various temperature 288.15–303.15K with the help of Non-Destructive Technique (Ultrasonic Technique). The data obtained also sheds light on intermolecular interactions between fertilizer-water and fertilizer-water-saline salts in view to find a way to control or minimalize the stated problem of soil salinity. The ultrasonic sound velocity (U) and density (ρ) measurements and their aligned properties (elastic, mechanical and thermal) find the wide applications in characterizing the physico-chemical behavior of liquid mixture.

EXPERIMENTAL DETAILS

1. *Chemicals Information*

Table 27.1: Shows the different chemicals used in view to perform the experiment.

Chemical Name	*Molecular Weight*	*CAS Number*	*Purchased From*	*Purity*
Sodium Chloride	58.44	7647–14-5	Himedia Lab. Pvt. Ltd., Mumbai	>> 99.8%
Sodium Sulfate	142.04	7757–86-6		
Double Distilled Water	18.02	NIL		
Triple Super Phosphate	370.11	65996–95-4		

2. *Apparatus Information*

Table 27.2: Shows the different apparatuses used in view to perform the experiment.

Name of Apparatus	*Purchased From*	*Uses*
2 MHz operating Digital Ultrasonic Velocity Interferometer	Vi Microsystems Pvt Ltd, Chennai	For the measurement of Ultrasonic sound velocity in liquid mixture.
10ml Specific Gravity Bottle	Enggific Engineering and Scientific, Hyderabad	For the determination of densities of the solutions.
Automatic Thermostatic Water Bath	Lab Hosp Pvt Ltd, Nagpur	For maintaining the experimental temperature of circulating water constant.

Defining Parameters

For calculated values of several elastic, mechanical and thermal properties the following defining relations reported in the literature are used:

(I) Surface Tension (σ): Surface tension describes the tendency of liquid surface at rest to shrink into the least surface area possible = $(6.3*10^{-4})\rho U^{3/2}$

(II) Internal Pressure (πi): Internal Pressure is a significant parameter which is used to understand structure and nature of intermolecular interaction in the liquid molecules = $\{T\alpha/k_T\}$

(III) Isothermal Compressibility (k_T): Isothermal compressibility is used to determine the compressible properties of water supply.
Pandey et al. Method (k_T) = $17.1*10^{-4}/(T^{4/9}U^2\rho^{1/3})$

(IV) Bulk Modulus (K): Bulk modulus is the reciprocal of adiabatic compressibility; it is used to measure the ability of substance = $\frac{1}{\beta}$

(V) Thermal Conductivity (k): Thermal conductivity is referring to the ability of material or substance to conduct or transfer heat = $\{3.0*(\varrho N_A/M)^{2/3}k_B U\}$

(VI) Specific Heat Ratio (γ): The simplified relation for Specific Heat Capacity as = $\left\{\frac{17.1}{T^{4/9} * \rho^{1/3}}\right\}$

RESULT AND DISCUSSION

Surface tension was used to interpret the strength of intermolecular interaction that exists in the solution. Between the liquid molecules, cohesive forces exist which are responsible for the variations in the surface tension. The increasing trend of surface tension (σ) with the concentration of solute and temperature indicates that a significant association in the solution.[7]

Sound properties have the tendency to irradiate the strength as well as kind of the interaction taking place in the corresponding experimental solutions. In the present work, the internal pressure (π_i) increases with an increase in the concentration of fertilizer, and the temperature for all three solvents. Which confirms there is an attractive force between the constituent components of liquid. This growing ilk of the internal pressure in all the solutions designates a good agreement of interaction between fertilizer-soil salt solutions as compared to fertilizer-water.[8]

Isothermal compressibility is a measure of relative fluctuations in volume. An examination of Table 27.3 reveals the trends in the isothermal compressibility (k_T) is declining with an intensification in the concentration of triple superphosphate fertilizer in water also in the aqueous NaCl and Na_2SO_4 solution of 0.2 mol-kg^{-1}. The diminution in isothermal compressibility values with an increase in the concentration of fertilizer (TSP) seems to be the result of a corresponding decrease in free volume and available volume.[9] The calculated values of isothermal compressibility's have been further used for the determination of specific heat ratio.

Table 27.3: The values of Surface Tension (σ), Internal Pressure (π_i), Isothermal Compressibility (k_T), Bulk Modulus (K) and Thermal Conductivity (k) of System TSP+ H_2O/NaCl/Na_2SO_4.

Conc. (mol-kg^{-1})	σ						k_T		
	(kg/m^3)			(Nm^{-2})			(m^{2}N^{-1})		
	H_2O	NaCl	Na_2SO_4	H_2O	NaCl	Na_2SO_4	H_2O	NaCl	Na_2SO_4
288.15K									
0.000	35331.82	35331.82	35331.82	4.90	4.90	4.90	6.42	6.42	6.42
0.002	35473.68	36407.59	37727.94	4.93	5.09	5.33	6.40	6.26	6.04
0.004	35563.86	36473.87	37807.41	4.94	5.11	5.34	6.39	6.24	6.03
0.006	35632.82	36541.78	37885.95	4.96	5.12	5.36	6.38	6.23	6.02
0.008	35753.23	36609.33	37964.30	4.98	5.13	5.37	6.35	6.22	6.01
0.010	35828.80	36697.29	38041.68	4.99	5.15	5.39	6.34	6.21	6.00
0.012	35922.62	36786.71	38119.23	5.01	5.16	5.40	6.33	6.19	5.99
0.014	35990.58	36854.03	38196.21	5.02	5.17	5.41	6.32	6.18	5.98
0.016	36068.63	36883.86	38272.98	5.03	5.18	5.43	6.30	6.18	5.97
0.018	36125.37	36948.45	38349.93	5.04	5.19	5.44	6.30	6.17	5.96
0.020	36222.07	37016.53	38404.45	5.06	5.20	5.45	6.28	6.16	5.95

Contd.

Table 27.3: The values of Surface Tension (σ), Internal Pressure (π_i), Isothermal Compressibility (k_T), Bulk Modulus (K) and Thermal Conductivity (k) of System TSP+ H_2O/NaCl/Na_2SO_4 (Contd.)

293.15K									
0.000	35859.88	35859.88	35859.88	5.06	5.06	5.06	6.24	6.24	6.24
0.002	36030.14	36870.76	38094.98	5.10	5.25	5.47	6.22	6.09	5.91
0.004	36104.36	36927.56	38175.75	5.11	5.26	5.49	6.21	6.08	5.9
0.006	36171.88	37001.10	38255.58	5.12	5.27	5.50	6.20	6.07	5.89
0.008	36251.80	37066.05	38312.80	5.14	5.28	5.51	6.19	6.06	5.88
0.010	36330.82	37131.47	38391.67	5.15	5.29	5.53	6.17	6.05	5.87
0.012	36385.24	37196.15	38448.19	5.16	5.30	5.54	6.17	6.04	5.87
0.014	36460.69	37268.06	38525.94	5.17	5.32	5.55	6.16	6.02	5.86
0.016	36536.82	37326.67	38604.23	5.19	5.33	5.56	6.14	6.01	5.85
0.018	36586.62	37401.91	38704.70	5.20	5.34	5.58	6.14	6.00	5.83
0.020	36668.47	37480.07	38783.03	5.21	5.36	5.60	6.13	5.99	5.82
298.15K									
0.000	36420.62	36420.62	36420.62	5.23	5.23	5.23	6.06	6.06	6.06
0.002	36529.49	37336.12	38604.90	5.25	5.40	5.64	6.05	5.93	5.76
0.004	36603.83	37404.09	38664.79	5.27	5.41	5.65	6.04	5.92	5.75
0.006	36653.00	37472.35	38723.57	5.28	5.43	5.66	6.03	5.91	5.75
0.008	36714.39	37542.33	38789.36	5.29	5.44	5.67	6.02	5.90	5.74
0.010	36791.00	37588.43	38868.14	5.30	5.45	5.69	6.01	5.89	5.73
0.012	36844.98	37638.43	38949.65	5.31	5.46	5.70	6.01	5.89	5.72
0.014	36900.55	37684.37	39029.89	5.32	5.47	5.72	6.00	5.88	5.71
0.016	36955.42	37752.57	39104.77	5.33	5.48	5.73	5.99	5.87	5.70
0.018	37010.53	37786.21	39167.24	5.34	5.48	5.74	5.99	5.87	5.69
0.020	37067.29	37848.01	39227.91	5.36	5.50	5.76	5.98	5.86	5.68
303.15K									
0.000	36704.40	36704.40	36704.40	5.36	5.36	5.36	5.95	5.95	5.95
0.002	36858.75	37592.17	38878.01	5.39	5.57	5.77	5.92	5.83	5.65
0.004	36910.39	37639.74	38960.83	5.40	5.57	5.78	5.92	5.82	5.64

Contd.

Table 27.3: The values of Surface Tension (σ), Internal Pressure (π_i), Isothermal Compressibility (k_T), Bulk Modulus (K) and Thermal Conductivity (k) of System TSP+ H_2O/NaCl/Na_2SO_4 (Contd.)

0.006	36958.70	37685.80	39042.63	5.41	5.58	5.80	5.91	5.81	5.63
0.008	37021.06	37734.99	39122.21	5.42	5.59	5.81	5.91	5.81	5.62
0.010	37072.90	37781.56	39203.60	5.43	5.60	5.83	5.90	5.80	5.61
0.012	37126.66	37828.59	39285.12	5.44	5.61	5.84	5.89	5.80	5.60
0.014	37181.35	37875.68	39365.15	5.45	5.61	5.86	5.89	5.79	5.59
0.016	37234.56	37917.35	39446.49	5.46	5.62	5.87	5.88	5.79	5.58
0.018	37286.25	37968.16	39527.01	5.47	5.63	5.89	5.88	5.78	5.57
0.020	37341.98	38014.64	39604.92	5.48	5.64	5.90	5.87	5.77	5.56

Elastic ilk of liquid can be best understood by Bulk Modulus (K) due to the hydrogen bonding form in the distinct components of the solutions intensifications with the bulk modulus. In the existing case, it is found that the bulk modulus increases with varying the concentration of fertilizer. As, water is a polar solvent and when salts and fertilizer are mixed, the well inter-Molecular interaction arose, follow-on in close packing of molecules. The calculated values of bulk modulus are listed in Table 27.4 which specifies the strong association amongst fertilizer and saline salts molecules as compared to distilled water and fertilizer. The bulk modulus of the solvent is lower than that of the solution and increases with an increase in the concentration of the fertilizer.[10]

In the present investigation, the increase in bulk modulus values with the temperature rise is observed. This supports the facts indicated by the variation in ultrasonic velocity with temperature. Ultrasonic velocity determination or measurement can be utilized to evaluate thermal conductivity theoretically. The theoretical value of thermal conductivity of solvent (water) shows good agreement with the literature data.[11,12]

From Table 27.4 it is observed that the evaluated value of thermal conductivity for triple super phosphate mixed in 0.2 molal concentration of salt solutions is more than that of the 0.2 molal salt solutions at all concentrations and temperature. The observed trend of thermal conductivity is: Water > Fertilizer + Saline Salts > Saline Salts

In the current investigation, both the ultrasonic velocity and density values increase with the increase in temperature and as per Bridgeman's relation, thermal conductivity directly depends on these two factors. The increase in thermal conductivity with an increase in concentration and temperature clear that the flow of energy is possible when molecules get close to each other. This means in the present system intermolecular interaction taking place. It is confirmed with the rise of velocity, density, and drop of free length values due to the close packing structure.

Table 27.4: The values of Bulk Modulus (K), Thermal Conductivity (k) and Specific Heat Ratio (γ) of System TSP+ H_2O/NaCl/Na_2SO_4.

Conc. (mol-kg^{-1})	K			k			γ		
	(kg/m^3)			($Wm^{-1}K^{-1}$)			$(K^{4/9})^{-1}(kg^{1/3}m^{-1})^{-1}$		
	H_2O	NaCl	Na_2SO_4	H_2O	NaCl	Na_2SO_4	H_2O	NaCl	Na_2SO_4
288.15K									
0.000	2147315500	2147321948	2147321948	0.6292	0.6292	0.6292	0.138027	0.138027	0.138027
0.002	2173480500	2205266719	2307871343	0.0841	0.0856	0.0876	0.137919	0.137396	0.136798
0.004	2192106686	2224726721	2322802241	0.0843	0.0857	0.0878	0.137880	0.137364	0.136755
0.006	2210703584	2229615318	2328579846	0.0844	0.0858	0.0879	0.137842	0.137331	0.136712
0.008	2226847866	2234607409	2334305503	0.0846	0.0859	0.0880	0.137790	0.137298	0.136670
0.010	2243489963	2239581280	2340023962	0.0847	0.0860	0.0881	0.137744	0.137266	0.136629
0.012	2261606018	2246232135	2345686504	0.0848	0.0862	0.0882	0.137702	0.137232	0.136588
0.014	2275534528	2252980305	2351364374	0.0849	0.0863	0.0884	0.137666	0.137200	0.136549
0.016	2288598783	2257955952	2357011928	0.0851	0.0863	0.0885	0.137619	0.137169	0.136510
0.018	2301729318	2259879398	2362651870	0.0851	0.0864	0.0886	0.137572	0.137135	0.136470
0.020	2314127374	2264596678	2368307046	0.0853	0.0865	0.0887	0.137527	0.137103	0.136432
293.15K									
0.000	2190879703	2190879703	2190879703	0.6354	0.6354	0.6354	0.137016	0.137016	0.137016
0.002	2217324518	2249335165	2350047306	0.0850	0.0863	0.0882	0.136903	0.136472	0.135820
0.004	2232868400	2264583030	2354083182	0.0851	0.0864	0.0883	0.136861	0.136454	0.135776
0.006	2249002609	2268933827	2359980717	0.0852	0.0865	0.0885	0.136827	0.136416	0.135734
0.008	2263521423	2274316915	2365825616	0.0853	0.0866	0.0885	0.136778	0.136388	0.135692
0.010	2279526666	2279175561	2369813608	0.0855	0.0867	0.0887	0.136731	0.136359	0.135652
0.012	2295525210	2284068257	2375611860	0.0856	0.0868	0.0888	0.136688	0.136332	0.135611
0.014	2310305998	2288919012	2379567536	0.0857	0.0869	0.0889	0.136646	0.136297	0.135572
0.016	2324108184	2294218528	2385298006	0.0858	0.0870	0.0890	0.136602	0.136277	0.135533
0.018	2341527525	2298703842	2391067121	0.0859	0.0871	0.0892	0.136566	0.136238	0.135494
0.020	2360186293	2304217788	2398678696	0.0860	0.0873	0.0893	0.136516	0.136195	0.135455
298.15K									
0.000	2237573686	2237573686	2237573686	0.6420	0.6420	0.6420	0.136045	0.136045	0.136045
0.002	2261473075	2292117579	2395933525	0.0858	0.0870	0.0890	0.135961	0.135543	0.134846
0.004	2277231793	2304353571	2396963955	0.0859	0.0871	0.0891	0.135921	0.135513	0.134803
0.006	2294021301	2309436561	2401148275	0.0860	0.0872	0.0892	0.135879	0.135483	0.134761
0.008	2307371415	2314540456	2405266400	0.0861	0.0874	0.0893	0.135836	0.135451	0.134719

Contd.

Table 27.4: The values of Bulk Modulus (K), Thermal Conductivity (k) and Specific Heat Ratio (γ) of System TSP+ H_2O/NaCl/Na_2SO_4.

0.010	2323501867	2319754422	2409972427	0.0862	0.0874	0.0894	0.135793	0.135422	0.134679
0.012	2340188477	2323049570	2415779639	0.0863	0.0875	0.0895	0.135753	0.135388	0.134639
0.014	2353136675	2326587689	2421817949	0.0864	0.0876	0.0896	0.135711	0.135359	0.134601
0.016	2366463651	2329876003	2427768544	0.0864	0.0877	0.0898	0.135669	0.135329	0.134561
0.018	2382465556	2334991639	2433271973	0.0865	0.0877	0.0899	0.135628	0.135315	0.134522
0.020	2400773042	2337522649	2437754681	0.0866	0.0878	0.0900	0.135585	0.135267	0.134484
303.15K									
0.000	2261908674	2261454293	2261908674	0.6454	0.6454	0.6454	0.135106	0.135106	0.135106
0.002	2282222345	2315644749	2421700500	0.0863	0.0874	0.0894	0.135021	0.134603	0.133937
0.004	2295241030	2326451087	2421114637	0.0864	0.0875	0.0895	0.134984	0.134572	0.133894
0.006	2310241988	2329845570	2427217099	0.0864	0.0876	0.0897	0.134951	0.134544	0.133853
0.008	2322527068	2333147327	2433261141	0.0865	0.0877	0.0898	0.134903	0.134511	0.133812
0.010	2339177160	2336645090	2439137922	0.0866	0.0877	0.0899	0.134864	0.134482	0.133772
0.012	2354356910	2339982356	2445174480	0.0867	0.0878	0.0900	0.134825	0.134448	0.133733
0.014	2368417486	2343283047	2451231992	0.0868	0.0879	0.0902	0.134785	0.134419	0.133693
0.016	2384323584	2346666351	2457166012	0.0869	0.0879	0.0903	0.134746	0.134390	0.133655
0.018	2397016404	2349595007	2463227199	0.0870	0.0880	0.0904	0.134708	0.134359	0.133616
0.020	2415693884	2353253872	2469221816	0.0870	0.0881	0.0905	0.134669	0.134329	0.133578

The variation of specific heat ratio of changeable weight fraction (0.002–0.02 mol-kg^{-1}) of fertilizer: Triple Super Phosphate in water and 0.2 mol-kg^{-1} aqueous solutions of NaCl and Na_2SO_4 at overall temperatures. The heat capacity ratio (γ) is decreasing, with the rise of temperature and fertilizer addition in the pure water and salt solutions. These results of specific heat ratios well support the increase of density with an increase in the concentration of solute fertilizer.[13] The order of variation in water and salt solution is observed as Na_2SO_4<NaCl<H_2O

CONCLUSION

Numerous mechanical, thermal and elastic parameters were calculated for triple superphosphate fertilizer in both water and saline salt solutions (NaCl and Na_2SO_4) at 288.15K, 293.15K, 298.15K, and 303.15K temperature by measuring the values of density and speed of sound. All parameters help to investigate the inter-molecular connections present between the molecules of triple superphosphate fertilizer-water and triple superphosphate fertilizer-saline salts. The influence of concentration on the different properties was observed and explained with the help of physicochemical behavior.

On the basis of resultant discussion, it was concluded that:

a. The variation in concentration, ilk of solute, ilk of the solvent, and its place actings a chief role in defining the kind of interactions going on in the solution.
b. It is further concluded that at higher concentrations the H-bonding is strong.
c. All the properties exhibit the maximum values for TSP fertilizer dissolved in Na_2SO_4 solution, coz it has a weak interaction with water molecules can bind with fertilizer molecules more excellently.
d. The trend of interaction occurred as: $(TSP+H_2O+Na_2SO_4) > (TSP+H_2O+NaCl) > (TSP+H_2O)$

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INNOVATIVE TRENDS IN PURE SCIENCES

NEEDS, CHALLENGES AND OPPORTUNITIES

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CHAPTER 21

PHOSPHATE COMPOUNDS DOPED WITH RARE EARTH IONS EXHIBITING LUMINESCENCE

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Abstract

This book chapter centers on the examination of luminescent materials compromising phos compounds as the host material and rare earth ions. The initial section commences with an overvi the luminescence phenomenon, providing a background study to establish context and understan Subsequently, we delve into a review of the commonly employed methodologies for synthesis context. As a result, this article primarily focuses on providing an overview of various phosphate – luminescent materials and explores contemporary developments and advancements in the fie luminescence.

Keywords: luminescence, phosphate, rare earth

Introduction

Luminescence is the ability of a body to produce light when subjected to electromagnetic radiati other forms such as energy released from chemical reaction or electrons. Examples: When the mat is stimulated by low – energy photons frequently ultraviolet radiations (photoluminescence), by ca rays (cathodoluminescence), by the strength of an electric field (electroluminescence), by X-rays (luminescence), and similar scenarios. The emitted light from a luminescent material manifests i visible segment of the electromagnetic spectrum but may also extend into the infrared (IR) or ultra (UV) regions. Luminescent materials are commonly referred to as "Phosphors" which comprise a lattice and a luminescent center often referred to as an "activator". Activators absorb incoming radia becoming elevated to an excited state. Subsequently, the excited state transitions back to the ground emitting radiation [1]. Thus, the host lattice is composed of at least one type of oxide, derived products such as sulphide, aluminate, alumino silicate, silicate, phosphate and others. Above al mentioned materials, Phosphate holds a crucial position among these materials, playing a significant in environmental systems. It is valued for its versatility, contributing to a variety of functions due notable attributes, including remarkable simplicity, low viscosity, high ultraviolet (UV) transmis excellent mechanical and thermal stability, isotropic refractive index, and simple synthesis[2,3].

Over the recent years, phosphate compound have garnered significant attention as materials for Pla Display Panels (PDPs). This is attributed to the fact that phosphors based on phosphates serves as cr luminescent hosts, exhibiting robust absorption in the Vacuum Ultraviolet (VUV) region (100-200 Additionally these, compounds showcase high chemical stability and are cost effective, fu contributing to their appeal for use in such applications [4]. Various rare – earth activated phosp materials have been recently explored for their application in the field of light – emitting diodes (LE Among these, mineral based phosphate materials have particularly garnered significant attention as p - luminescent materials. Phosphate based phosphors are widely recognized for their suitability in sol state lighting applications. Phosphate, due to its medium energy level, high damage threshold, ro thermal and chemical stability, cost effective raw materials, and relatively simple preparation conditi stands out as an ideal host for white LEDs (W-LEDs) [5].

Methodology

Various synthesis methods have been reported to date for the production of phosphate based materials. Each method are described below:

1. Melt Quenching Technique

The melt quenching method is one of the oldest techniques used for producing phosphors, including phosphate based phosphors for glass or white LEDs (w- LEDs) preparation. In this method, starting materials and minerals are carefully mixed and melted in a furnace. The resulting melt solution is then poured onto a brass plate and promptly pressed with another plate to create a thin, transparent glass. The color of the obtained glass is influenced by the starting materials and the dopant used in the preparation process. The rate of quenching is crucial factor affecting glass formation; a faster rate of melt quenching contributes to a more efficient glass formation [6, 7].

2. Wet Chemical method

The wet chemical method is a chemical based – approach that utilizes materials typically in the form of nitrates, as they readily dissolve in water. This method encompasses various techniques such as sol – gel method and co precipitation method, all falling under the broader category of "Wet Chemical Synthesis". The sol- gel method, considered a primary wet chemical method, involves the transformation of a solution into a gel, allowing for the controlled synthesis of materials. This approach offers versatility in tailoring material properties. Overall, the wet chemical method represents a diverse set of techniques, each contributing to the synthesis of material with specific characteristics [8].

The role of Phosphates in various luminescent domains

Extensive research has been conducted in research years on luminescent materials based on phosphates, driven by their exceptional spectroscopic characteristics and crystalline structure. In recent studies, Lanthanides (Ln) – activated rare – earth phosphate has emerged as a noteworthy and practical optical fluorescent probe. This is attributed to its unique luminescent behavior, particularly in suitable activators like Eu^{3+}, Tb^{3+}, Gd^{3+}, etc. Consequently, it serves as an effective alternative to conventional semiconductor quantum dots containing cadmium. Moreover, Ln- activated large band gap nanocrystals also provide a robust crystal environment for the dopant ions, leading to an elevated photoluminescence (PL) quantum yield (QY). Among numerous phosphate based phosphors, $LaPo_4$ (LAP) has gained paramount importance in various fields, serving as laser materials, catalysts, and versatile biological labels, heat resistant materials, catalysts and photon up conversion materials [9].

Conclusion

The proposed review article comprehensively examines the recent advancements of phosphate – based materials in various luminescent applications. The detailed discussion encompasses different synthesis methods for preparing phosphate based phosphor materials, including the wet chemical method, combustion method and sol gel method. The research emphasizes that enhancing the photoluminescence (PL) of phosphate phosphors requires materials with properties suitable for solid state lighting applications. This phosphors hold potential for applications in workforce, clinical dosimetry and environmental dosimetry, with a particular focus on achieving extremely low dose dosimetry. The investigation underscores the necessity for materials highly sensitive to ionizing radiations in this context.

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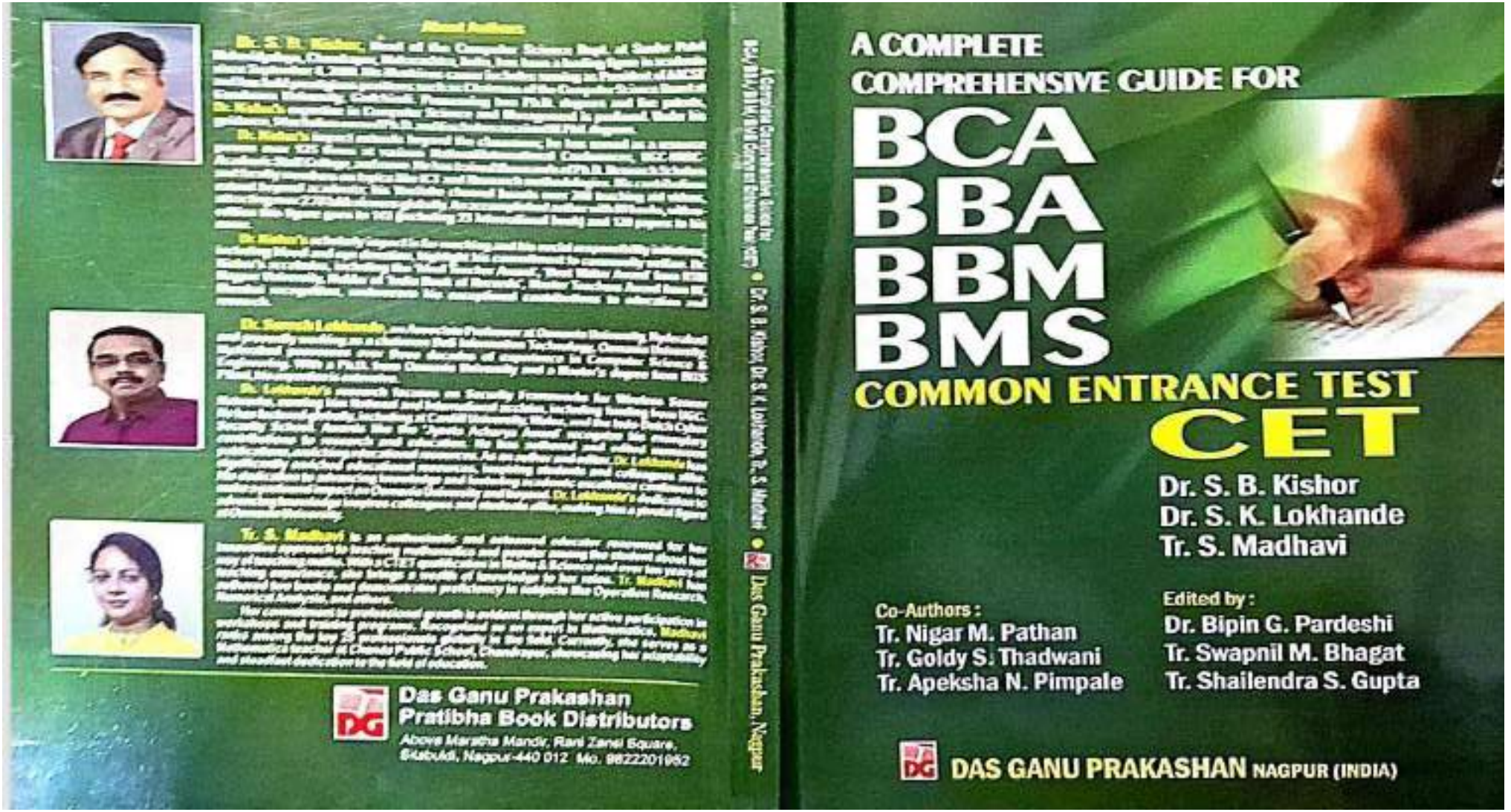

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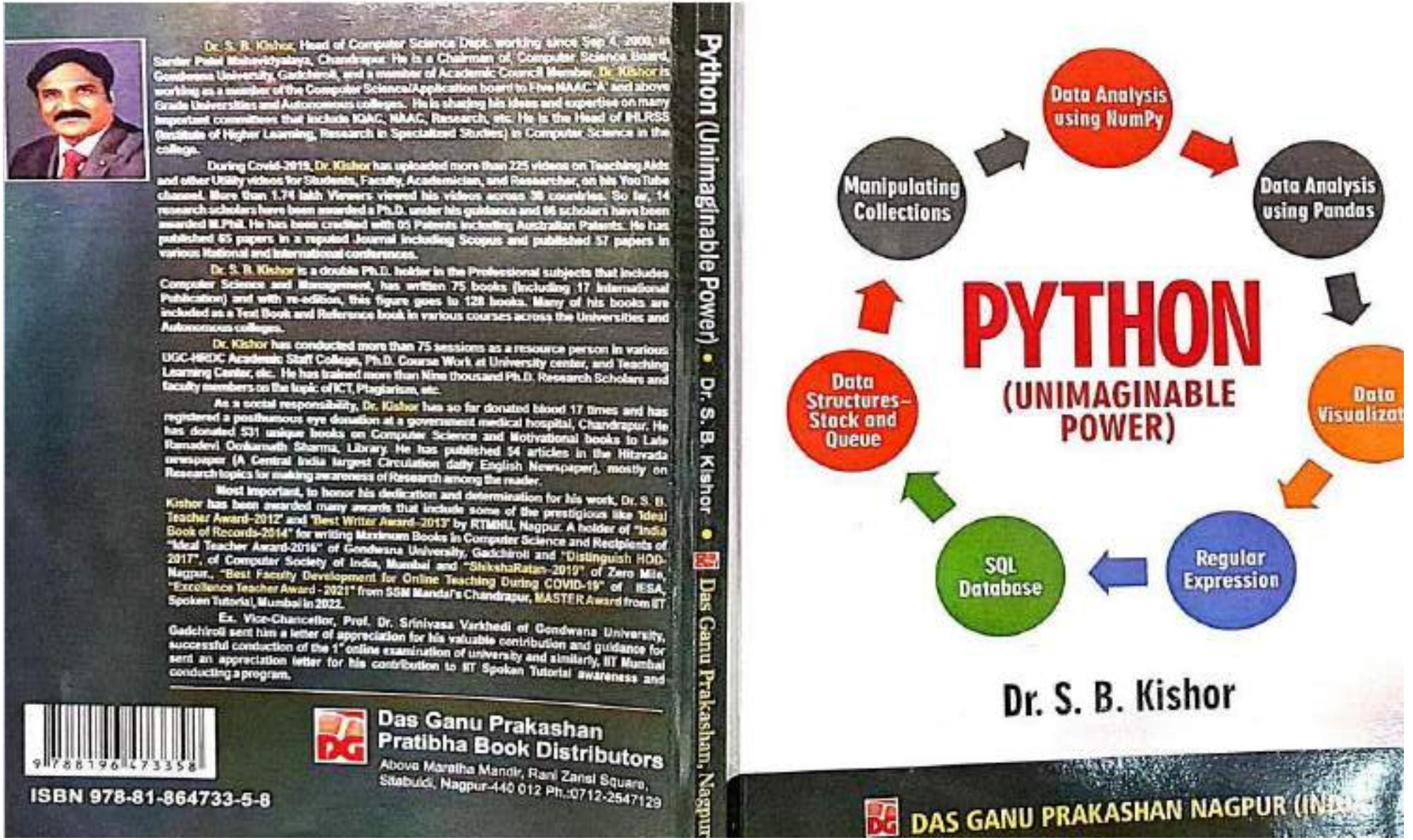
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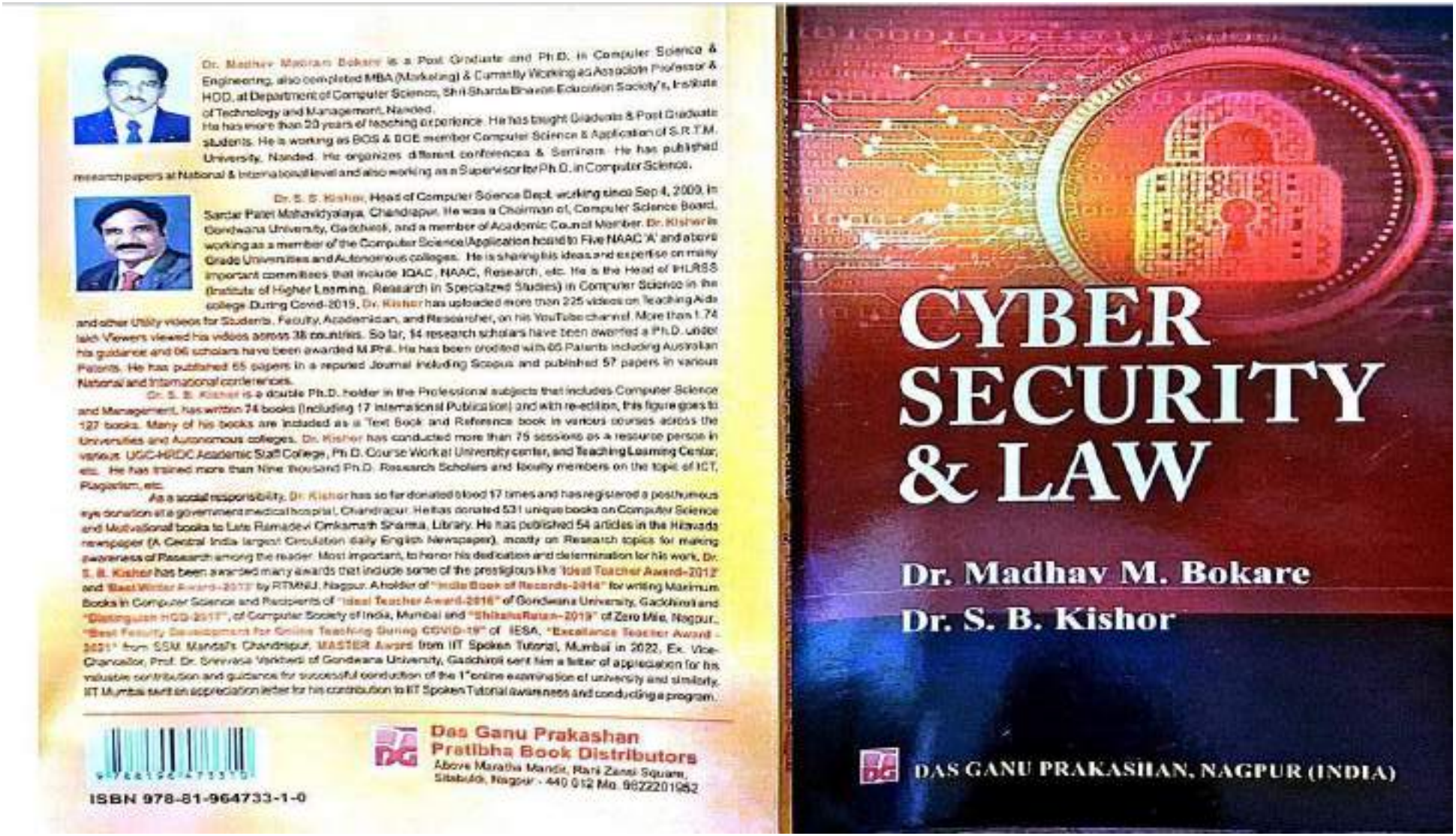

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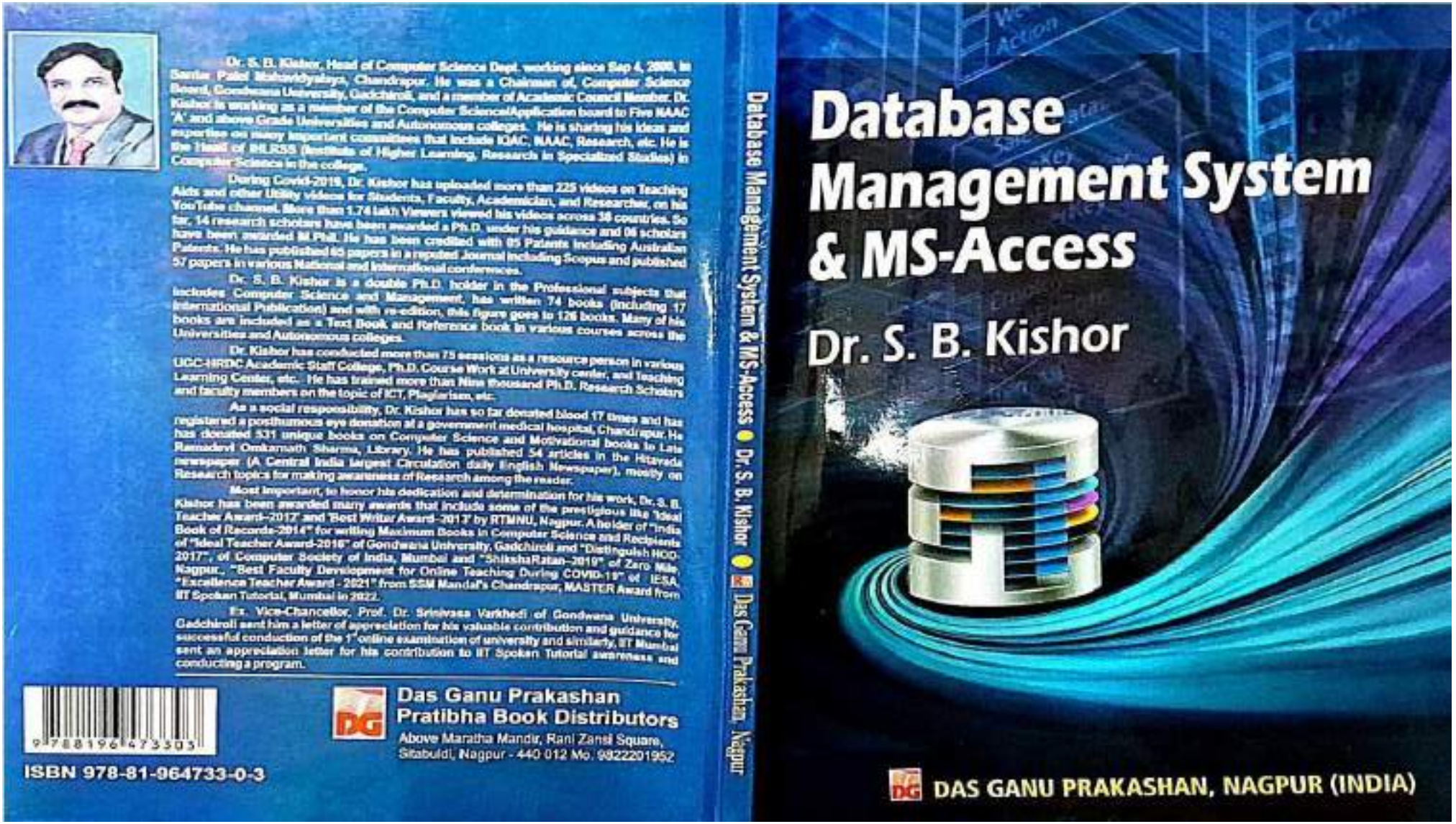

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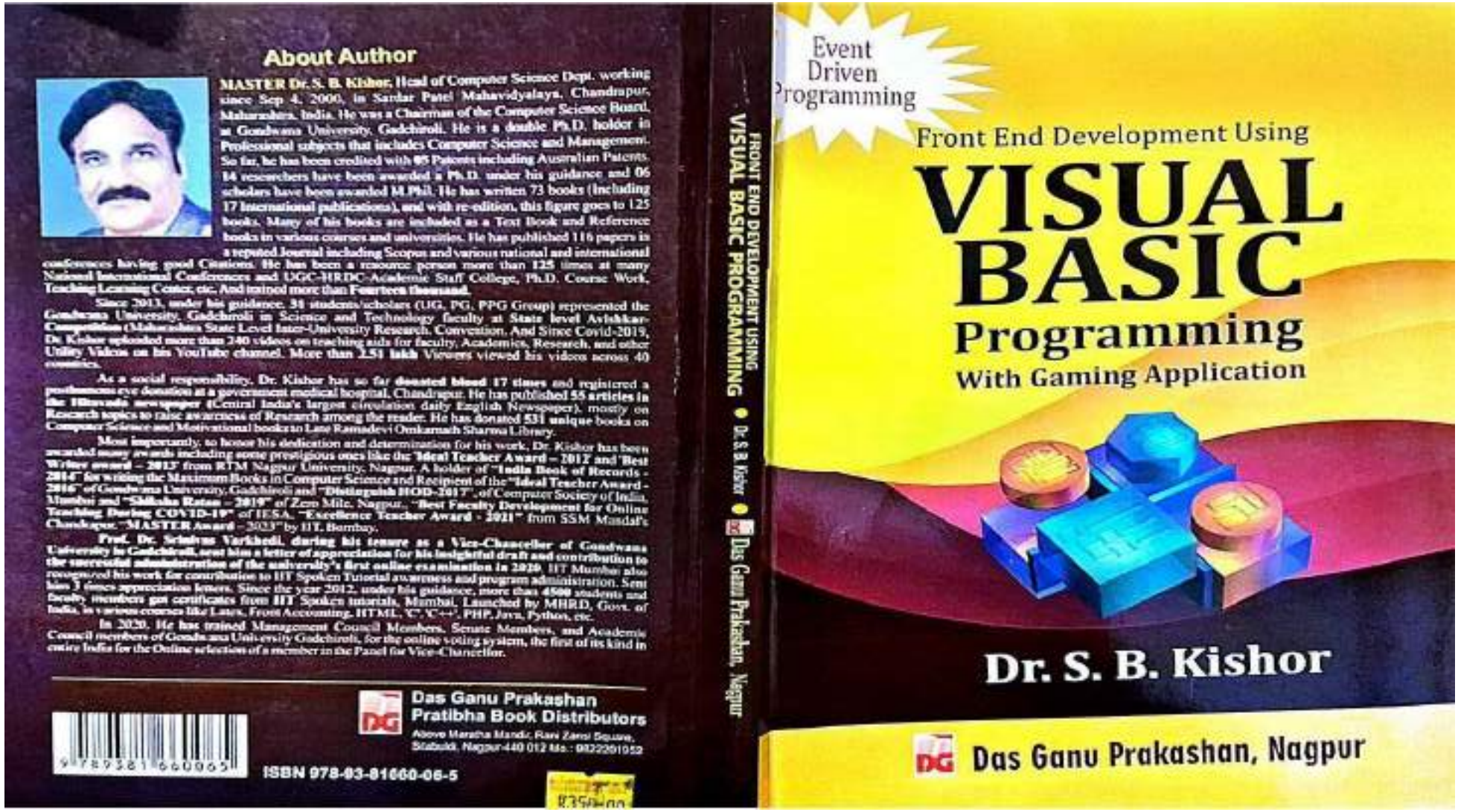

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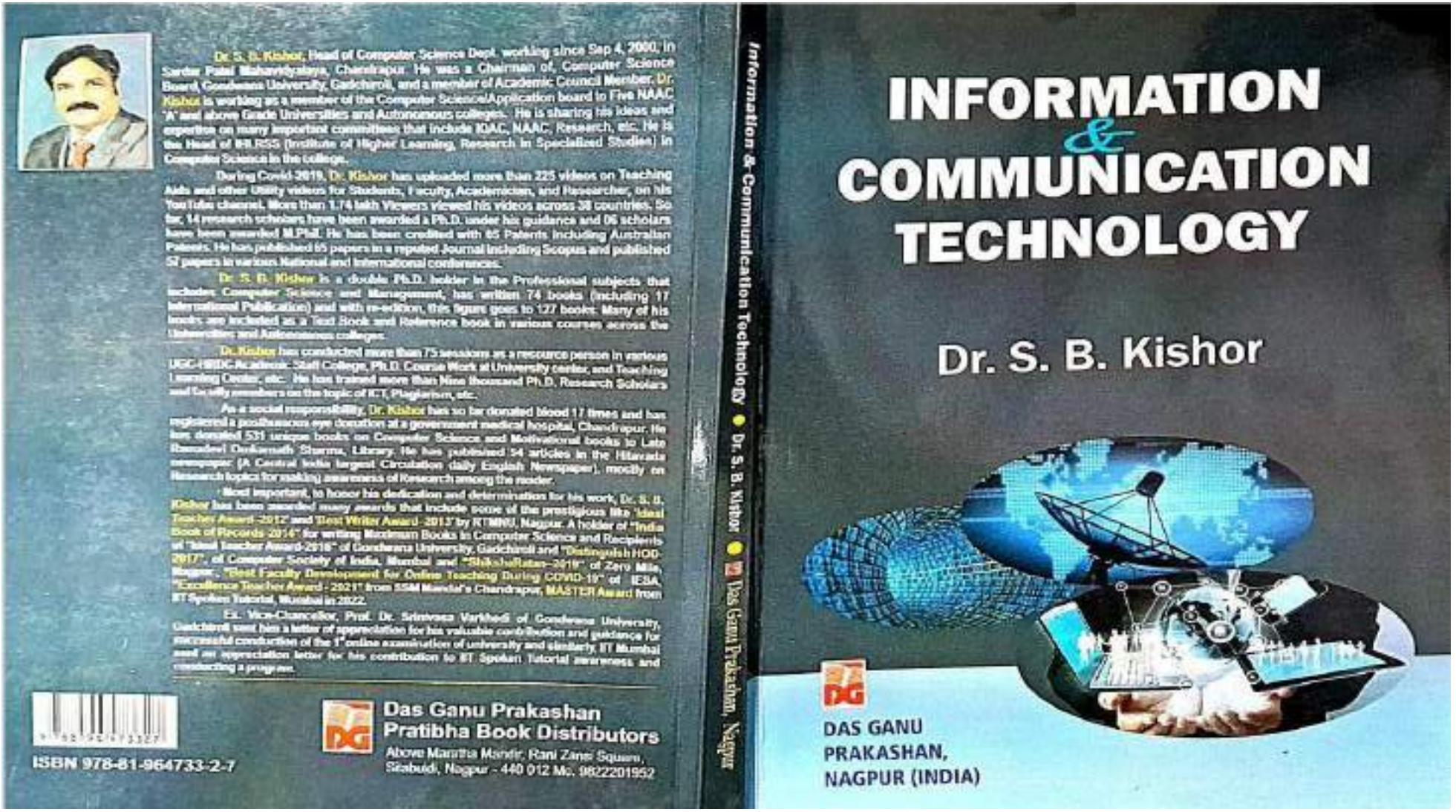

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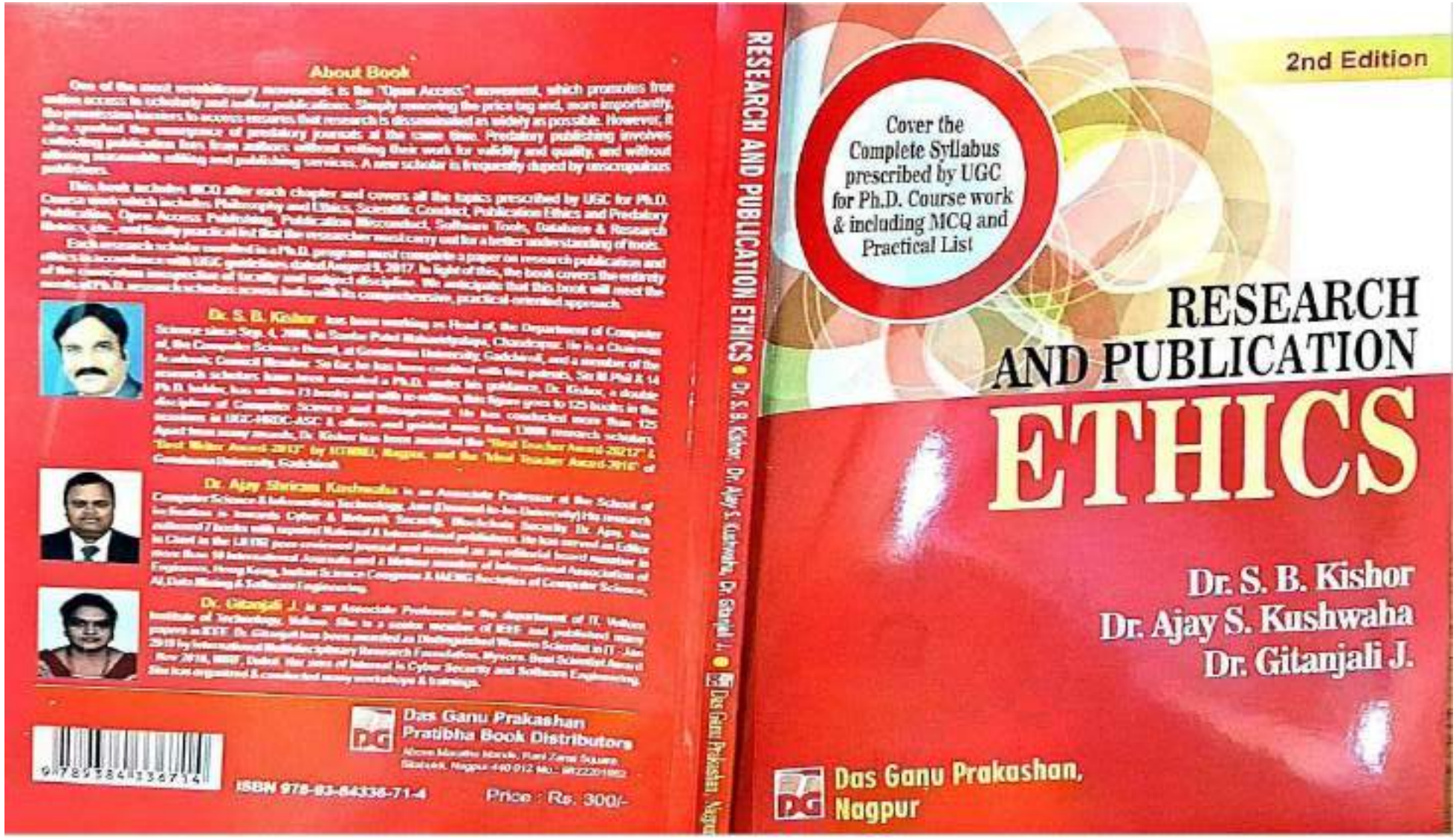

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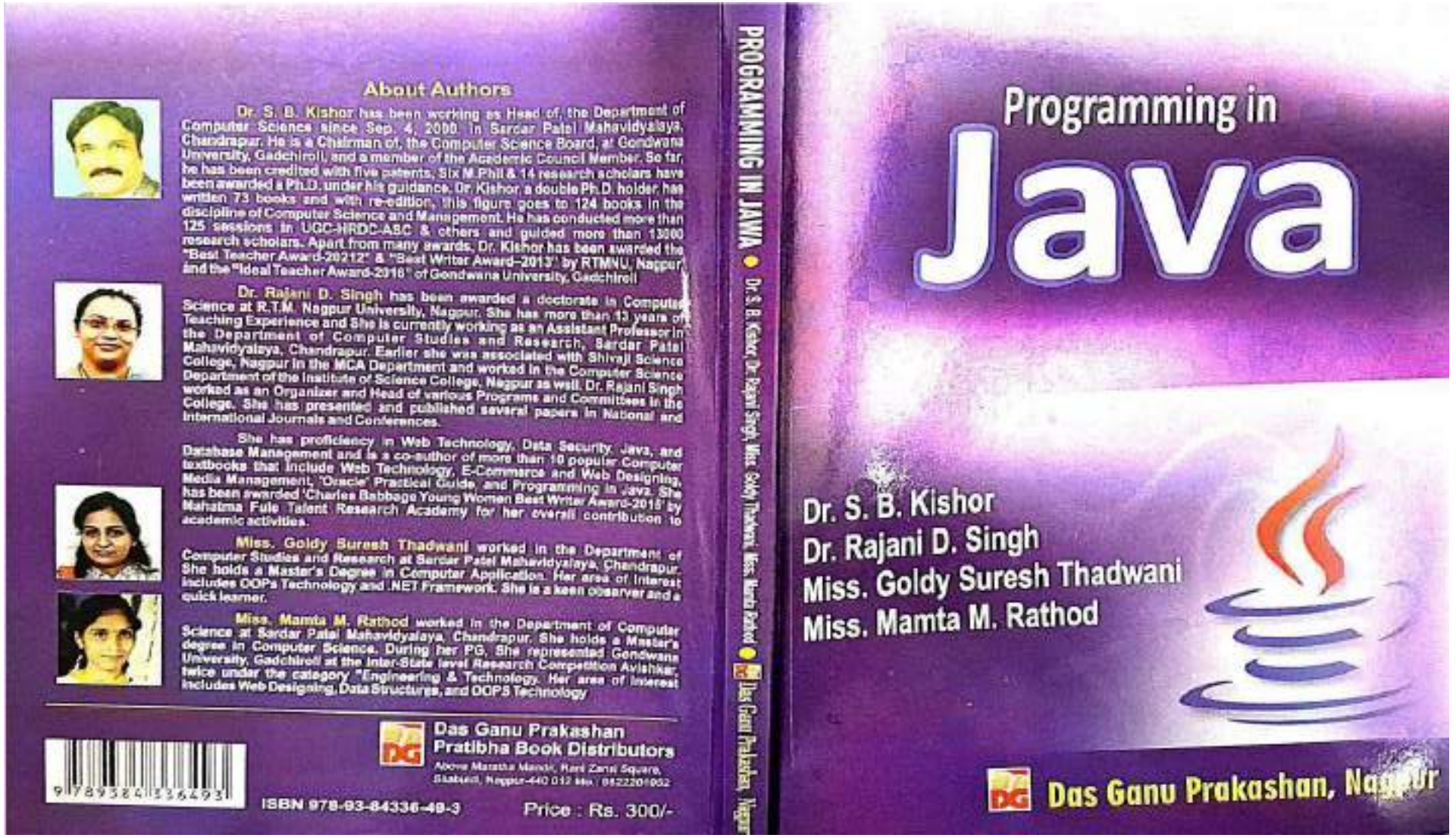

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